Supporting Information for

Quantum Tunneling Mediated Low-Temperature Synthesis of Interstellar Hemiacetals

Jia Wang,[1,2+] Anatoliy A. Nikolayev,[3+] Joshua H. Marks,[1,2] Mason Mcanally,[1,2] Valeriy N. Azyazov,[4] André K. Eckhardt,[5*] Alexander M. Mebel,[6*] Ralf I. Kaiser[1,2*]

[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*

[4] *Lebedev Physical Institute, Samara 443011, Russia*

[5] *Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, Bochum 44801, Germany*

[6] *Department of Chemistry and Biochemistry, Florida International University, Miami, Florida 33199, USA*

[*]Corresponding Authors: Andre.Eckhardt@ruhr-uni-bochum.de, mebela@fiu.edu, ralfk@hawaii.edu

[+] Contributed Equally

METHODS

Experimental. The experiments were conducted in a stainless steel chamber under ultrahigh vacuum (UHV) conditions at pressures of about 8×10^{-11} Torr using turbomolecular pumps (Osaka, TG1300MUCWB and TG420MCAB) backed by a dry scroll pump (Edwards GVSP30).[1] Acetaldehyde (Sigma Aldrich, anhydrous, ≥99.5% purity) and methanol (Sigma-Aldrich, HPLC grade) samples were stored in separate glass vials connected to a high vacuum chamber at pressures of a few 10^{-8} Torr and repeatedly frozen and thawed using liquid nitrogen to remove residual atmospheric gases. To prepare each ice mixture, methanol and acetaldehyde vapors were deposited via separate glass capillary arrays onto a polished silver substrate, which was mounted on a cold finger maintained at 5.0 ± 0.1 K using a two-stage closed-cycle helium refrigerator (Sumitomo Heavy Industries, RDK-415E). The substrate can be rotated in the horizontal plane or translated vertically with a rotational feedthrough or a linear translator, respectively. The deuterated samples used in the experiment are acetaldehyde-d_3 (CD_3CHO, CDN isotopes, ≥98 atom % D), acetaldehyde-d_4 (CD_3CDO, Sigma Aldrich, ≥99 atom % D), methanol-d_3 (CD_3OH, Sigma Aldrich, ≥98 atom % D), and methanol-d_4 (CD_3OD, Cambridge Isotope Laboratories Inc., 99.96% D atom). Utilizing a He-Ne laser (CVI Melles Griot, 25-LHP-230) of 632.8 nm wavelength at an angle of incidence equal to 4°, the thickness of each ice was monitored online and in situ via laser interferometry.[2] The average refractive index of the acetaldehyde–methanol ice was determined to be 1.32 ± 0.04 based on the refractive index of amorphous acetaldehyde (n = 1.303)[3] and that of methanol ice (n = 1.33 ± 0.04).[4] By accounting for the densities of methanol (0.779 g cm^{-3}) and acetaldehyde (0.787 g cm^{-3}),[5] the ice thicknesses of 750 ± 30 nm were calculated. Note that thicker ices (2300 ± 200 nm) were used for CH_3CHO−CH_3OH and CD_3CDO−CD_3OD systems to obtain better signal-to-noise infrared spectra (Figure 2). The infrared spectra of the ice mixtures were collected in the 6000–500 cm^{-1} region using a Fourier transform infrared (FTIR) spectrometer (Nicolet 6700) operated at a spectral resolution of 4 cm^{-1}. The ratio of acetaldehyde to methanol in the ice mixture was determined to be (1.1 ± 0.3):1 based on integrating the infrared features of acetaldehyde at 1128, 1350, and methanol at 2827, 3270 cm^{-1} and their absorption coefficients of 6.6×10^{-19}, 1.1×10^{-18}, 5.3×10^{-18}, and 1.01×10^{-16} cm $molecule^{-1}$, respectively.[4,6,7]

After the deposition, temperature-programmed desorption (TPD) was conducted by heating the sample from 5 K to 320 K at a rate of 0.5 K $minute^{-1}$. During the TPD phase, either IR spectra

were used to track chemical changes induced by the thermal reaction or the sublimed molecules from the ices were analyzed using vacuum ultraviolet (VUV) photoionization reflectron time-of-flight mass spectrometry (PI-ReToF-MS). The pure IR spectra of 1-methoxyethanol and fully deuterated 1-methoxyethanol-d8 at 150 K were achieved after the sublimation of both reactants (Figure 2). In PI-ReToF-MS mode, sublimed hemiacetal molecules were photoionized by pulsed VUV photons at 10.49 eV (118.222 nm), 9.70 eV (127.819 nm) and 9.20 eV (134.765 nm), which were generated by resonant or non-resonant four-wave mixing processes (Table S5). The third harmonic (355 nm) of a pulsed Nd:YAG laser (Spectra-Physics, Quanta Ray Pro 250-30) was used to generate the 10.49 eV (118.222 nm) photons via frequency tripling in pulsed gas jets of Xe gas. To produce 9.70 eV light, a second harmonic (532 nm) from another pulsed Nd: YAG laser (Spectra-Physics, Quanta Ray Pro 270-30) was used to pump a dye laser (Sirah, Cobra-Stretch) containing Rhodamine 610/640 dye mixture (0.17/0.04 g L^{-1} ethanol) to obtain 606.948 nm (2.04 eV), which undergoes frequency tripling to generate 202.316 nm (ω_1, 6.13 eV) (β-BaB_2O_4 (BBO) crystals, 44° and 77°). The third harmonic (355 nm) of an Nd:YAG laser pumped a dye laser (Coumarin 480, 0.4 g L^{-1} ethanol) to produce 484.982 nm (ω_2, 2.56 eV). The 9.20 eV light was produced in pulsed jets of Xe gas with ω_2 = 638.667 nm and ω_1 = 222.566 nm, which was obtained via a double frequency of 445.132 nm from a dye laser. The ω_1 and ω_2 lights were spatially and temporally overlapped in a non-linear medium of Kr or Xe for the generation of 9.70 eV or 9.20 eV photons. Using a biconvex lithium fluoride lens (ISP Optics) in an off-axis geometry, the VUV photons (ω_{vuv}) were spatially separated from the dye lasers (ω_1 and ω_2) and other wavelengths generated via multiple resonant and non-resonant processes ($3\omega_1$; $3\omega_2$; $2\omega_1 + \omega_2$) and passed at 2.0 ± 0.5 mm above the ice surface for ionizing the sublimed molecules. The resulting ions were extracted and separated based on their mass-to-charge (*m/z*) ratio before reaching the microchannel plate (MCP) detector (Jordan TOF Products, Inc.). The ion signal generated from MCP is first amplified by a preamplifier (Ortec 9305), converted to 4 V with a 100 MHz discriminator (3.2 ns bins, 30 Hz), and then recorded with a dedicated multichannel scaler (FAST ComTec, MCS6A) with accumulation times of 3600 sweeps (2 minutes) for each recorded mass spectra.

Computational. All computations were carried out with Gaussian 16, Revision C.01.[8] For geometry optimizations of neutral conformers of 1-methoxyethanol (**1**) and their ions and their frequency computations, the density functional theory (DFT) B3LYP functional[9-11] was employed utilizing the Dunning correlation consistent split valence basis set cc-Pvtz.[12] Based on these

geometries, the corresponding frozen-core coupled cluster[13-16] CCSD(T)/cc-pVTZ, and CCSD(T)/cc-pVQZ single point energies were computed and extrapolated to complete basis set limit[17] CCSD(T)/CBS with B3LYP/cc-pVTZ zero-point vibrational energy (ZPVE) corrections. The adiabatic ionization energies were computed by taking the ZPVE corrected energy difference between the neutral and ionic species that correspond to similar conformations. As in general the difference between heavier isotopologues and standard isotopologues in the zero-point vibrational energy is marginal, we used the ZPVEs of standard isotopologues for IE calculations and assumed them to be the same for our experiments with heavier isotopologues. The electric field of ion optics lowers the ionization energy by 0.03 eV,[18] which was considered during the IE error analysis (Table S3). The computed Cartesian coordinates and vibration frequencies for the structures of 1-methoxynethanol are listed in Table S6. For the calculation of the Gibbs free energies depicted in Figure S4, all geometries were optimized at the B3LYP/cc-pVTZ level of theory and augmented CBS-QB3[19] energies (Table S7). Potential energy surfaces for the reaction of methanol and acetaldehyde in mixed ices were computed using the ωB97X-D density functional[20] with the 6-311G(d,p) basis set. Implicit solvent effects were taken into account by applying the universal continuum SCRF SMD model[21] considering methanol below its freezing temperature as a solvent, with the dielectric constant 82.17[22] the refractive index 1.35.[23] Note that this value of the refractive index is close to 1.32 ± 0.04 for the acetaldehyde–methanol ice in the present study. The variation of the dielectric constant had very little effect on the reaction energetics. Optimized Cartesian coordinates and harmonic frequencies involved in the potential energy surfaces illustrated in Figure 5 and S6 are detailed in Table S8.

Calculations of the tunneling transmission coefficient

At low temperatures, reactions that involve the transfer of light atoms, such as hydrogen atoms, may exhibit quantum mechanical tunneling. The ratio of thermally averaged quantum tunneling probability to quasiclassical transmission probability defines the tunneling transmission coefficient κ(T). For a one-dimensional truncated parabolic-type barrier, the Skodje–Truhlar tunneling transmission coefficient κ(T) can be calculated using the following equation:[24]

$$\kappa(\mathrm{T}) = \begin{cases} \dfrac{h\nu/(2k_{\mathrm{B}}T)}{\sin\left[h\nu/(2k_{\mathrm{B}}T)\right]} - \dfrac{\exp\left[\left(\frac{1}{k_{\mathrm{B}}T} - \frac{2\pi}{h\nu}\right)V_b\right]}{2\pi k_{\mathrm{B}}T/(h\nu) - 1} & \dfrac{2\pi k_{\mathrm{B}}T}{h\nu} > 1 \quad (a) \\ \dfrac{V_b}{k_{\mathrm{B}}T} & \dfrac{2\pi k_{\mathrm{B}}T}{h\nu} = 1 \quad (b) \\ \dfrac{\exp\left[\left(\frac{1}{k_{\mathrm{B}}T} - \frac{2\pi}{h\nu}\right)V_b\right]}{1 - 2\pi k_{\mathrm{B}}T/(h\nu)} & \dfrac{2\pi k_{\mathrm{B}}T}{h\nu} < 1 \quad (c) \end{cases} \qquad \text{(S1)}$$

where h is the Planck constant, ν the absolute value of the imaginary frequency of the transition state, k_{B} the Boltzmann constant, and T the temperature of reaction. The intrinsic barrier V_{b} is given by:[24]

$$V_b = \quad V_{max} - \max\left[0, \Delta V\right] \qquad \text{(S2)}$$

where ΔV is the value of the potential of products relative to the reactants, V_{max} is the value of the potential at its maximum relative to reactants. At temperature of 113 K, κ(T)s are calculated based on their barriers, reaction energies, and imaginary frequencies at the transition states. These tunneling transmission coefficients range from 214 to several orders of magnitude higher, corroborating the fact that the reaction is dominated by tunneling.

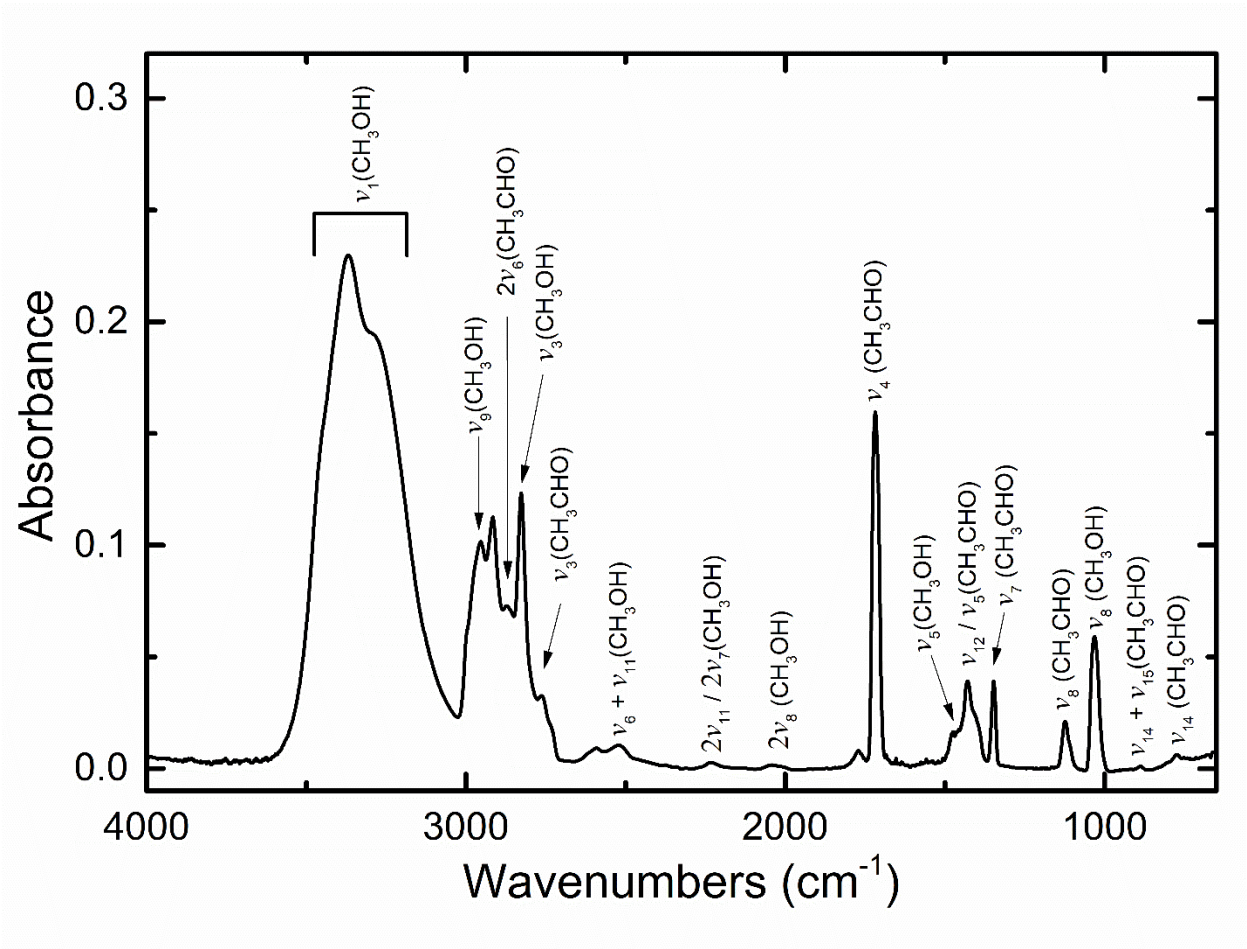


Figure S1. FTIR spectrum of an CH_3CHO–CH_3OH ice after deposition at 5 K.

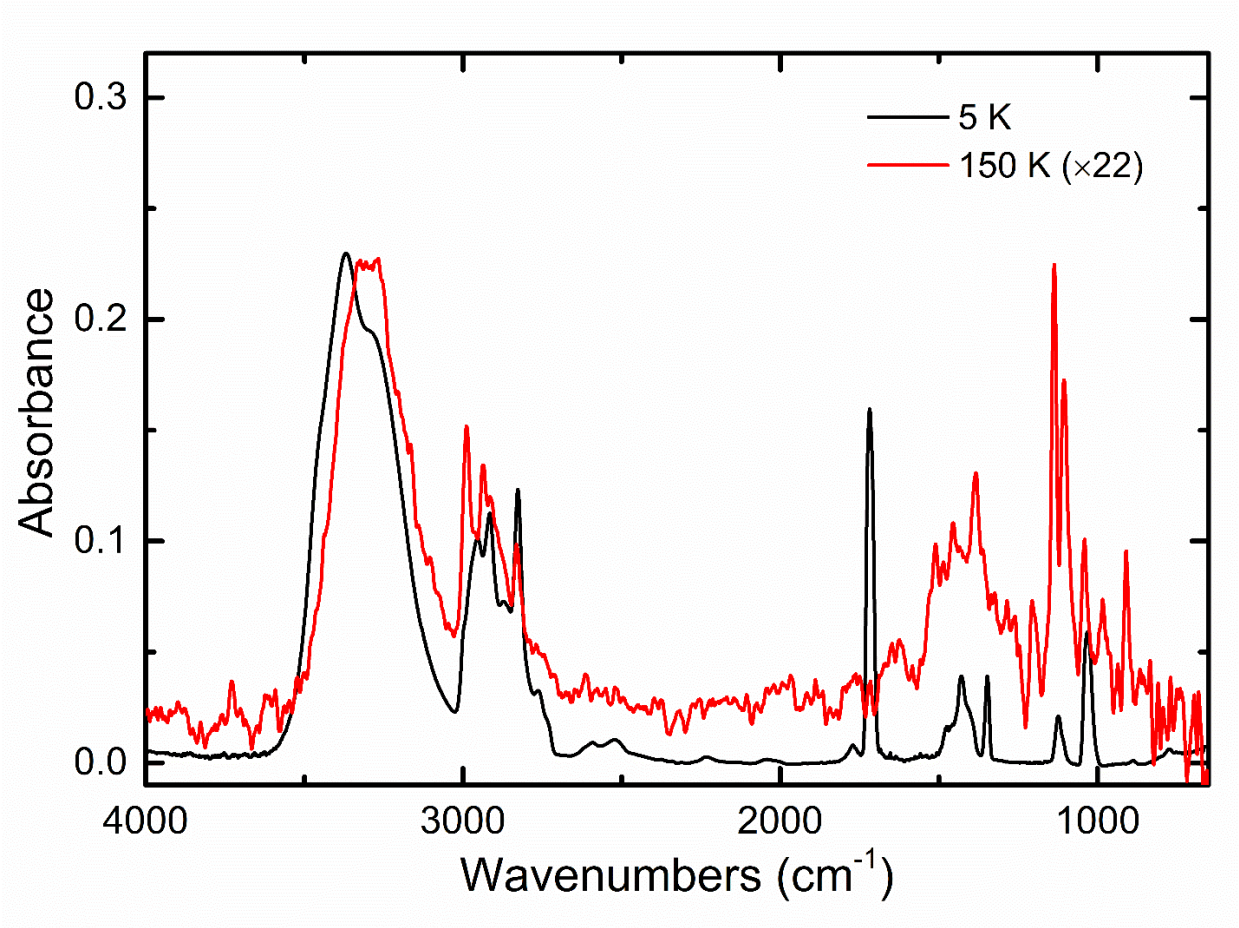


Figure S2. Overlay of FTIR spectra of CH_3CHO–CH_3OH ice measured at 5 K (black) and 150 K (red).

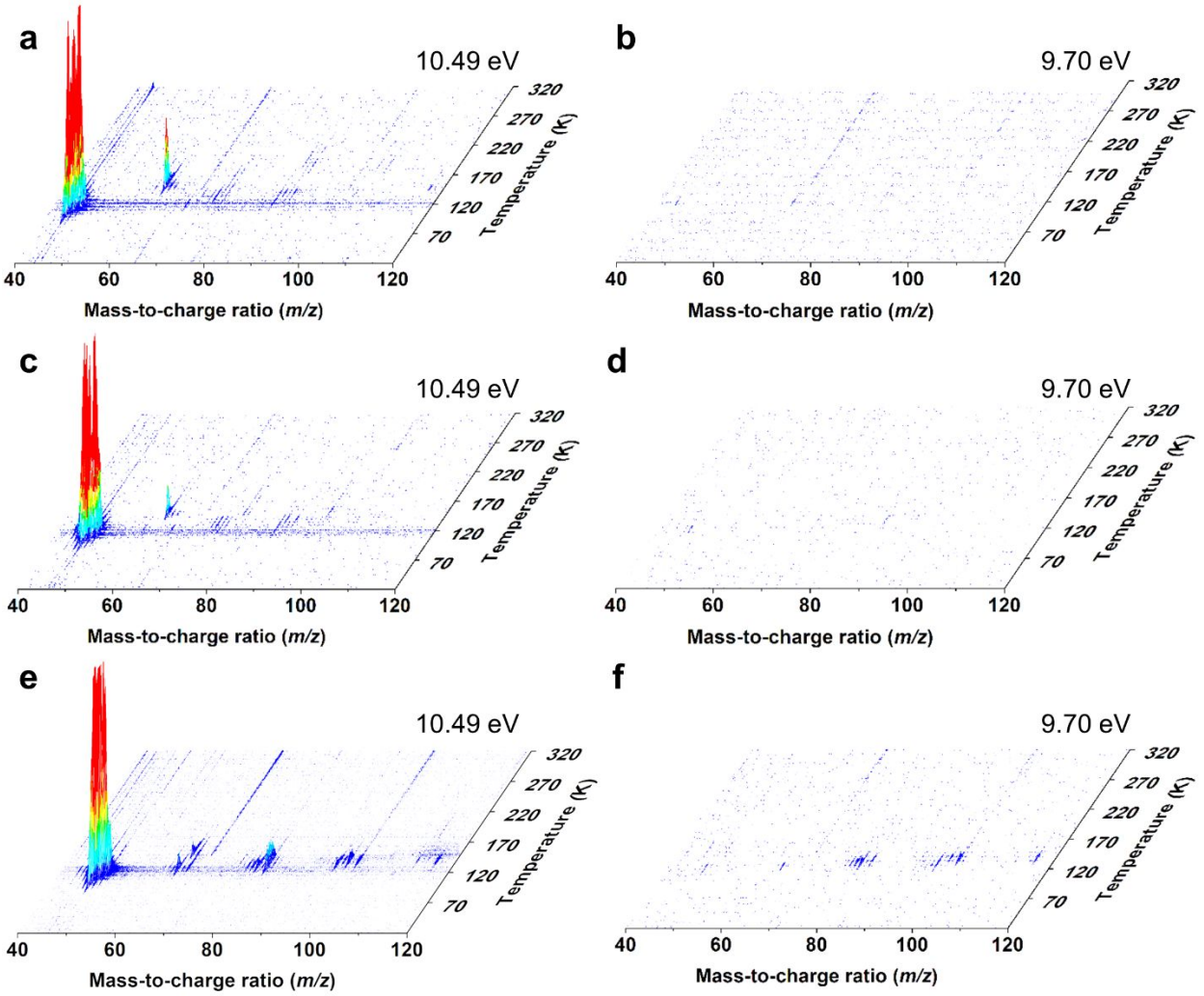


Figure S3. PI-ReToF-MS mass spectra collected during the temperature-programmed desorption (TPD) phase of the acetaldehyde–methanol ice mixtures. The CH_3CHO–CH_3OH ice was photoionized at 10.49 eV (**a**) and 9.70 eV (**b**); CD_3CHO–CH_3OH ice was photoionized at 10.49 eV (**c**) and 9.70 eV (**d**); CD_3CDO–CD_3OH ice was photoionized at 10.49 eV (**e**) and 9.70 eV (**f**).

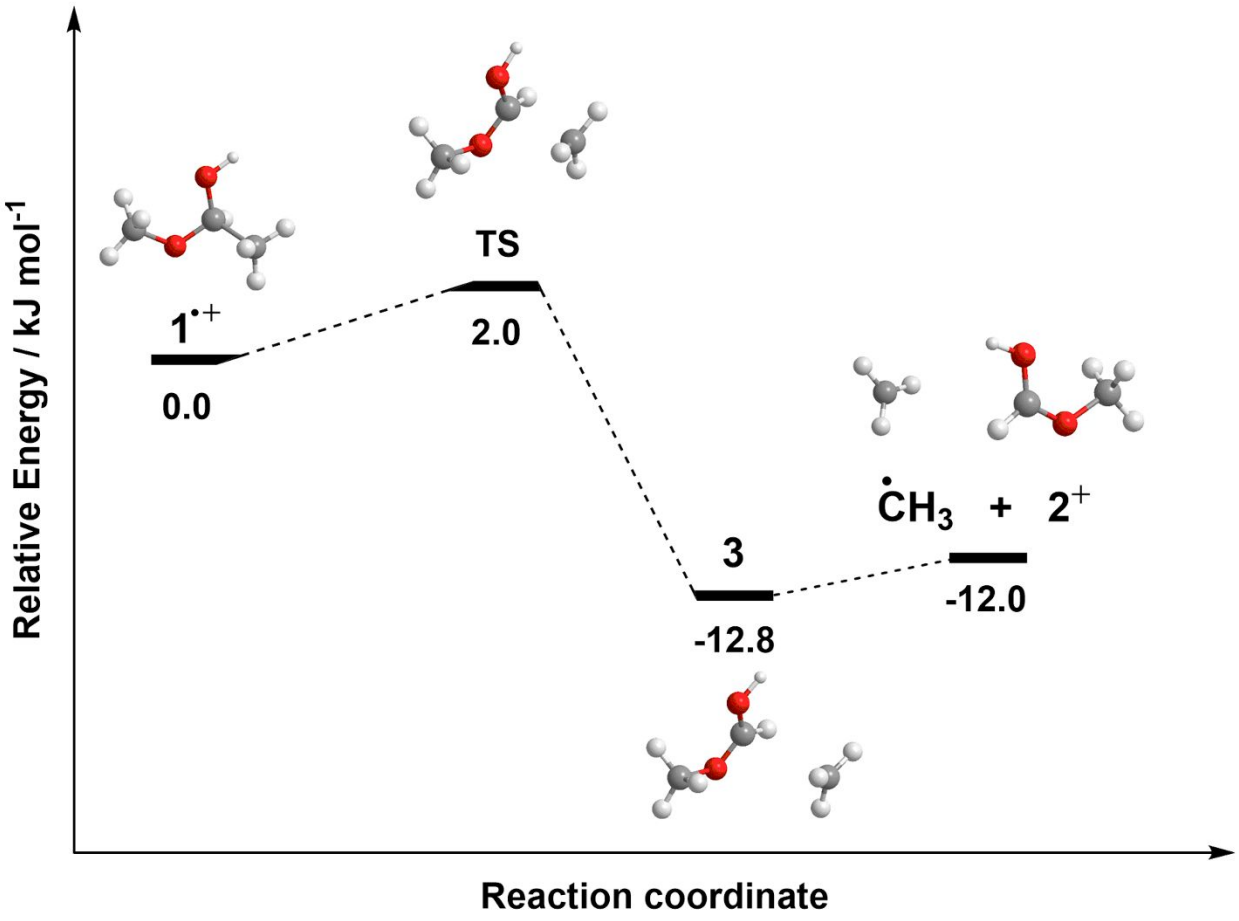


Figure S4. Calculated dissociation pathways of the 1-methoxyethanol radical cation ($\mathbf{1}^{\bullet+}$), leading to the methyl radical and fragment ion, hydroxymethylmethylium ($\mathbf{2}^{+}$). The Gibbs free energies calculated (151 K) at the CBS-QB3 level are given in kJ mol^{-1} relative to the 1-methoxyethanol radical cation ($\mathbf{1}^{\bullet+}$).

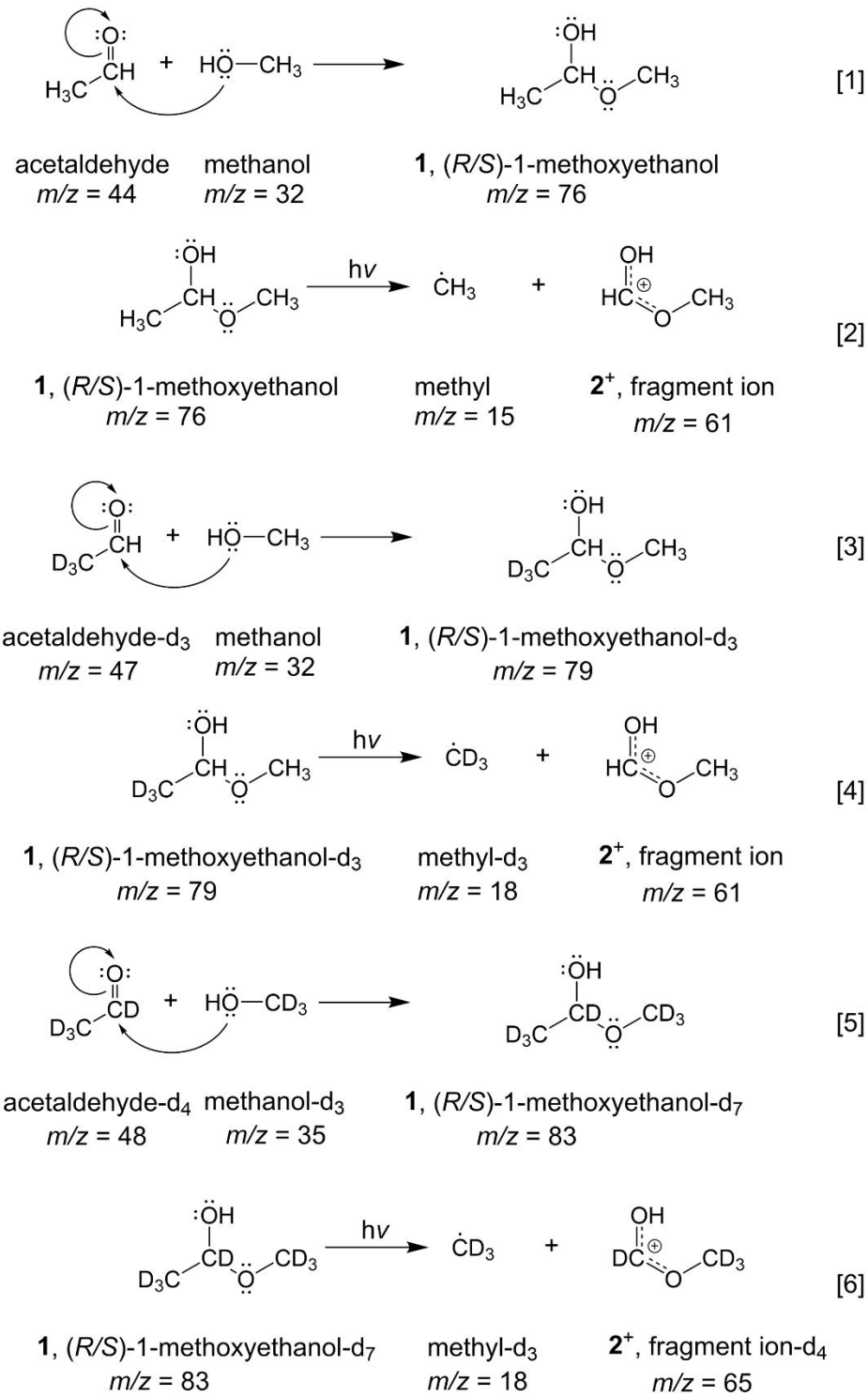


Figure S5. Formation mechanisms of 1-methoxyethanol (**1**) via nucleophilic addition and its photoionization fragment, hydroxymethylmethylium ($\mathbf{2}^+$). Reactions [1] and [2] for CH_3CHO–CH_3OH ice; reactions [3] and [4] for CD_3CHO–CH_3OH ice; reactions [5] and [6] for CD_3CDO–CD_3OH ice.

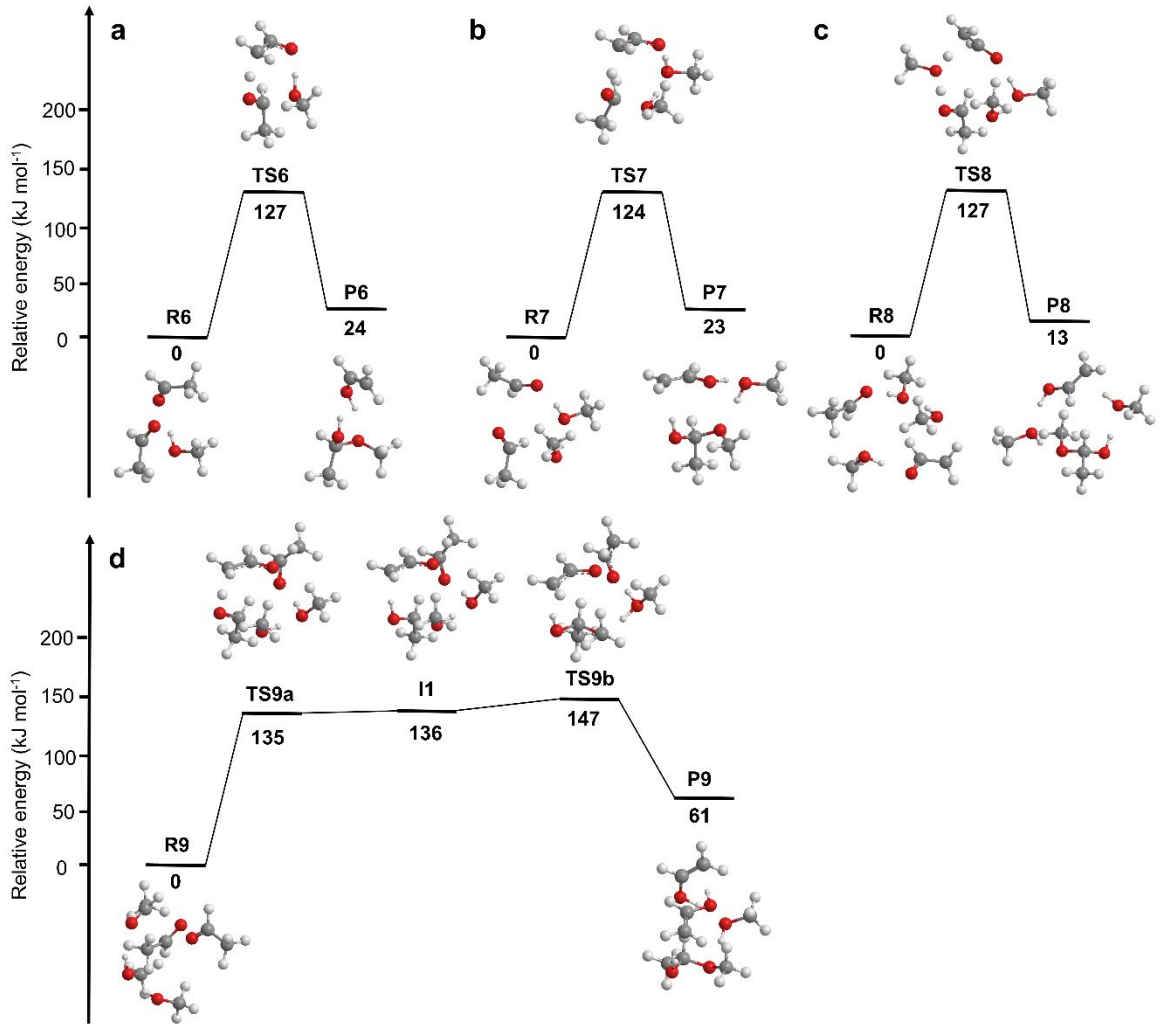


Figure S6. Potential energy surfaces of the reactions between various combinations of acetaldehyde (CH_3CHO) and methanol (CH_3OH) molecules leading to the formation of 1-methoxyethanol (**1**). Panels **a** to **d** illustrate the reaction pathways for the systems $(CH_3CHO)_2$–CH_3OH, $(CH_3CHO)_2$–$(CH_3OH)_2$, $(CH_3CHO)_2$–$(CH_3OH)_3$, and $(CH_3CHO)_3$–$(CH_3OH)_2$, respectively. The reactants, transition states, intermediates, and products are labelled as "**R**", "**TS**", "**I**" and "**P**", respectively. Energies, computed at the SCRF/SMD//ωB97X-D/6-311G(d,p) + ZPVE level of theory, are shown in kJ mol^{-1} and are relative to the energy of the reactants. The atoms are depicted with a color code of white for hydrogen, gray for carbon, and red for oxygen.

Table S1. Absorption peaks observed in CH_3CHO–CH_3OH ices after deposition at 5 K.

Absorption position (cm^{-1})	
CH_3OH	Assignment[25,26]
3402, 3261, 3048	ν_1
2957	ν_9
2917	$2\nu_4$ / $2\nu_5$ / $2\nu_{10}$
2826	ν_3
2598	$\nu_4 + \nu_{11}$
2521	$\nu_6 + \nu_{11}$
2233	$2\nu_{11}$ / $2\nu_7$
2041	$2\nu_8$
1476	ν_4
1455	ν_5
1031	ν_8
CH_3CHO	Assignment[27]
2869	$2\nu_6$
2761	ν_3
1768	$2\nu_9$
1716	ν_4
1427	ν_{12} / ν_5
1392	ν_6
1347	ν_7
1123	ν_8
887	$\nu_{14} + \nu_{15}$
775	ν_{14}

Table S2. Absorption peak positions (cm^{-1}) of 1-methoxyethanol (**1**) in CH_3CHO–CH_3OH and CD_3CDO–CD_3OD ices measured after the sublimation of acetaldehyde and methanol. Assignment labels: stretching (ν), bending (δ), rocking (ρ).

CH_3CHO–CH_3OH ice		
Experimental (this work)	Reported Position	Assignment [c]
3310		ν(OH)
2988		ν(CH)
2932		ν(CH)
2832		ν(CH)
1511		δ(CH)
1456		δ(CH)
1384		δ(CH)
1204	1210[a]	$\rho(CH_3)$
1137	1140[a], 1150[b]	ν(CO)
1107	1087[b]	ν(CO)
909	920[a], 917[b]	$\rho(CH_3)$
CD_3CDO–CD_3OD ice		
Experimental (this work)	Reported Position	Assignment [c]
2461		ν(OD)
2244		ν(CD)
2215		ν(CD)
2069		ν(CD)
1274		δ(CD)
1256		δ(CD)
1141		ν(CO)
1097		ν(CO)
978		$\rho(CD_3)$

[a] From Meadows et al.,[28] measured in methanol.
[b] From Dutta et al.,[29] calculated at B3LYP/6-31++G(d,p) level of theory.
[c] Calculated at the B3LYP/cc-pVTZ level of theory.

Table S3. Error analysis of adiabatic ionization energies (IE) and relative energies (*Δ*E) of 1-methoxyethanol (**1**); IEs and *Δ*E were computed at the CCSD(T)/CBS//B3LYP/cc-pVTZ level of theory including the zero-point vibrational energy corrections. Their computed Cartesian coordinates and vibrational frequencies are shown in Table S6. The IE ranges are calculated based on the electrical effect of −0.03 eV and computed IE error limits of −0.05 - +0.03 eV.[30]

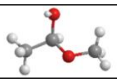
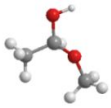
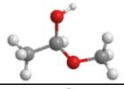
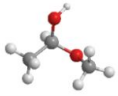
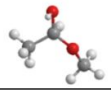
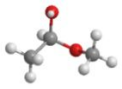
Isomer	Structure	*Δ*E (kJ mol^{-1})	Dipole moment (Debye)	Computed IE (eV)	IE range after error analysis (eV)	Corrected IE with electric field effect (eV)
1a		0	0.37	9.98	9.93 – 10.01	9.90 – 9.98
1b		10.2	1.99	9.76	9.71 – 9.79	9.68 – 9.76
1c		6.6	2.12	9.73	9.68 – 9.76	9.65 – 9.73
1d		7.2	0.20	9.72	9.67 – 9.70	9.64 – 9.72
1e		14.1	1.75	9.72	9.67 – 9.70	9.64 – 9.72
1f		17.2	2.35	9.62	9.57 – 9.65	9.54 – 9.62

Table S4. Calculated Gibbs free energies (kJ mol^{-1}) for the structures involved in the dissociation pathways of 1-methoxyethanol, 1-methoxyethanol-d_3, and 1-methoxyethanol-d_7 cations. The Gibbs free energies calculated at the CBS-QB3 level are relative to the corresponding 1-methoxyethanol cation (**1**$^{\cdot+}$).

	Reactant (**1**$^{\cdot+}$)	Transition state (**TS**)	Complex (**3**)	Methyl radical and **2**$^{+}$
1-methoxyethanol cation	0.0	2.0	-12.8	-12.0
1-methoxyethanol-d_3 cation	0.0	3.6	-10.0	-8.5
1-methoxyethanol-d_7 cation	0.0	2.5	-11.1	-9.6

Table S5. Parameters for the generation of vacuum ultraviolet (VUV) light. The uncertainty for VUV photon energies is less than 0.0001 eV.

VUV energy (eV)	10.49 ($3\omega_1$)	9.70 ($2\omega_1 - \omega_2$)	9.20 ($2\omega_1 - \omega_2$)
VUV wavelength (nm)	118.222	127.819	134.765
Nonlinear medium	Xenon	Krypton	Xenon
ω_1 wavelength (nm)	355	202.316	222.566
Nd:YAG output (nm)	355	532	355
Dye laser output (nm)	-	606.948	445.132
Dye	-	Rhodamine 610/640 (0.17/0.04 g L^{-1} ethanol)	Coumarin 450 (0.2 g L^{-1} ethanol)
ω_2 wavelength (nm)	-	484.982	638.667
Nd:YAG output (nm)	-	355	532
Dye laser output (nm)	-	484.982	638.667
Dye	-	Coumarin 480 (0.4 g L^{-1} ethanol)	DCM (0.3 g L^{-1} DMSO)

Table S6. Cartesian coordinates for structures of 1-methoxyethanol. B3LYP/cc-pVTZ optimized Cartesian geometry (Å), electronic energies (hartree) and vibrational frequencies (cm^{-1}) & intensities (km mol^{-1}), zero-point vibrational energies (ZPVE) (hartree), extrapolated CCSD(T)/CBS energies (hartree) and adiabatic ionization energies (IE) at CCSD(T)/CBS level of theory.

1a

C	1.647038	–0.821182	–0.010227
C	0.424238	0.007841	0.328106
H	1.776570	–0.864635	–1.093537
H	1.532016	–1.839703	0.358062
H	2.534857	–0.376363	0.435978
O	0.564738	1.362405	–0.056893
H	0.775499	1.381035	–0.997884
O	–0.680506	–0.604913	–0.290563
H	0.264574	0.056167	1.411399
C	–1.936466	–0.074033	0.105511
H	–2.093665	–0.198903	1.182970
H	–2.699612	–0.633227	–0.431100
H	–2.020081	0.986020	–0.141838

E = –269.6821552
E[CCSD(T)/CBS] = –269.2985145
ZPVE = 0.1124990

Frequency	Intensity
125.3641	3.6050
180.1028	3.4604
227.1570	0.7761
284.7352	2.1192
343.8847	82.8704
391.3748	25.2400
535.5502	10.6963
565.8097	24.8806
840.9693	9.2036
907.9046	65.5176
1052.4975	81.1241
1070.1458	34.1794
1118.2683	120.4363
1145.3900	140.0426
1177.9719	1.5567
1218.8900	24.4913
1306.3715	13.4142
1382.2524	14.2715

1410.6997	22.1698
1433.4828	60.3724
1473.2606	2.7108
1484.6364	0.9629
1487.1137	6.3180
1495.8970	6.5346
1513.8741	7.0383
2989.5222	43.1353
3000.8652	57.5555
3035.6276	13.2766
3058.7598	40.5221
3102.8858	27.1003
3116.9759	23.3948
3122.4663	17.7593
3780.6383	20.8598

1a-d_8

Frequency	Intensity
98.1193	1.3743
146.4724	3.6522
165.6843	0.4119
244.3285	13.6234
254.9121	40.3063
344.1516	9.9886
458.2172	6.9165
524.1276	20.9629
705.1611	1.7651
755.9242	6.5977
857.6289	38.8253
880.8878	17.6963
913.8787	7.2581
945.5429	26.6681
1008.3837	10.9410
1041.0891	12.7320
1066.5611	23.6642
1070.1544	12.1966
1074.4516	3.4305
1089.6373	10.5514
1093.3914	10.4779
1105.6532	70.6995
1135.2762	123.3380
1160.0427	52.1267
1253.5156	116.5193
2147.8376	36.9228
2181.8387	3.9567
2211.2097	32.3647

2263.5260	25.9051
2297.0023	13.6068
2311.0230	15.0989
2314.6021	7.4509
2751.1325	13.3162

1a^{+}

C	1.621825	–0.768144	–0.030704
C	0.500052	0.161037	0.309487
H	1.803488	–0.787883	–1.105652
H	1.405116	–1.778975	0.312773
H	2.519340	–0.421933	0.484879
O	0.581029	1.458073	–0.150942
H	1.144126	1.524285	–0.940889
O	–0.714017	–0.258508	–0.470053
H	0.221012	0.185470	1.360714
C	–1.981693	–0.206441	0.132858
H	–1.936057	–0.376260	1.207237
H	–2.607336	–0.918528	–0.412272
H	–2.404152	0.792595	–0.077257

E = –269.3306659
E[CCSD(T)/CBS] = –268.9286049
ZPVE = 0.1094960

Frequency	Intensity
56.2687	4.7597
106.9933	15.9249
225.2812	0.3918
297.7567	12.8753
340.8625	5.0425
362.5005	4.5039
441.1438	43.9397
528.5316	74.1453
624.5186	38.2128
866.1477	12.8284
919.6565	39.9703
1026.9209	11.3672
1050.2738	38.4849
1077.5016	49.9444
1150.7270	41.3304
1174.5588	24.1295
1293.2245	45.2903
1338.0519	17.4897
1350.3114	77.0186

1390.1917	22.5697
1414.0514	4.6325
1430.8676	65.2497
1466.9328	17.9346
1475.8854	16.6938
1485.8855	20.5422
2912.1783	159.4211
3035.5016	14.6195
3040.2284	7.5360
3108.7388	1.5545
3117.9061	3.0805
3128.6702	5.7240
3130.4551	9.2008
3694.4238	260.1255

1b

C	1.357275	–0.943760	0.056520
C	0.370359	0.190634	0.245816
H	0.948032	–1.881043	0.432412
H	2.280169	–0.730526	0.594752
H	1.580686	–1.050694	–1.004215
O	0.956300	1.352410	–0.266643
H	0.283544	2.042034	–0.267801
O	–0.846617	–0.017682	–0.458541
H	0.122515	0.314292	1.313311
C	–1.781013	–0.844707	0.205627
H	–2.697589	–0.822952	–0.380055
H	–1.996366	–0.477401	1.216510
H	–1.439624	–1.882608	0.278901

E = –269.6777963
E[CCSD(T)/CBS] = –269.2943452
ZPVE = 0.1122190

Frequency	Intensity
95.3946	1.4173
188.8079	0.7842
216.2003	5.7505
302.9790	48.5681
327.5976	57.1886
410.1554	5.6335
459.6311	16.3741
566.5570	8.4638
840.4638	21.0482
932.9774	34.4070
1026.0729	87.5825

1111.8091	41.7130
1117.1322	95.0237
1162.3109	114.8680
1178.8777	3.9660
1228.1389	21.4197
1290.0048	101.1700
1392.9336	26.6415
1397.4542	4.3488
1451.7210	50.2164
1474.6595	7.1062
1485.5003	12.2565
1489.2787	1.4923
1499.0469	2.7380
1512.4443	5.7598
2911.5101	75.4386
2977.0583	64.3646
3022.9218	52.3801
3044.6035	13.0753
3110.1904	32.2490
3112.5942	14.6982
3120.4844	18.8039
3800.9425	29.9916

1b-d_8

Frequency	Intensity
78.9068	0.7782
143.5790	0.8345
157.5072	2.7860
229.0961	57.2821
282.1733	3.1494
359.0458	2.5525
402.7982	12.0660
515.0491	4.2512
705.0685	7.0611
781.2713	13.0344
835.7372	35.6328
889.1456	3.5184
917.2890	4.9051
949.2732	8.5935
1017.9023	26.6883
1021.4142	21.1813
1064.2227	11.8753
1069.8934	13.0312
1076.6716	5.4089
1079.2845	1.5255
1090.0584	0.2395

1113.4743	73.4463
1146.6728	151.1557
1185.0840	103.5173
1277.5961	79.0462
2135.0992	18.0364
2144.7676	74.9279
2186.7944	2.6744
2240.7916	33.8483
2302.8864	17.0364
2305.9410	8.5286
2312.8158	9.2077
2766.0157	20.0331

1b^{+}

C	–0.922645	1.341289	0.014363
C	–0.395224	–0.239808	0.409061
H	–0.121619	2.003632	0.325028
H	–1.834026	1.460690	0.589054
H	–1.083595	1.314341	–1.058051
O	–1.425531	–1.059023	0.162400
H	–1.262726	–1.643782	–0.598342
O	0.710361	–0.509499	–0.286389
H	–0.249664	–0.100431	1.494531
C	1.972167	0.113408	0.066636
H	2.720125	–0.669023	–0.034919
H	1.944445	0.498006	1.083359
H	2.168760	0.902103	–0.658745

E = –269.3339565
E[CCSD(T)/CBS] = –268.9325881
ZPVE = 0.1092140

Frequency	Intensity
87.7447	3.4675
139.4058	1.3396
220.5534	0.0763
256.9591	9.1757
303.5157	112.3772
352.7757	35.5306
366.7758	5.5021
536.2020	34.4015
552.4660	21.1152
885.8645	9.2572
901.1724	40.9329
932.5115	78.4570

995.5942	18.0749
1124.6151	27.6146
1148.1654	8.4374
1179.1749	103.1539
1249.7105	79.1694
1302.3013	7.0858
1329.2031	7.3998
1346.9602	39.3949
1438.4595	13.1323
1444.6245	9.1500
1459.1170	13.4405
1470.5811	15.9534
1491.0785	52.3045
2914.3048	18.8587
3045.3880	11.5419
3070.1137	4.9311
3135.4645	1.9959
3157.3667	13.5646
3202.9978	0.6771
3208.9001	3.1325
3689.1964	268.2465

1c

C	1.649122	–0.786742	–0.033557
C	0.406929	–0.001080	0.315308
H	1.552874	–1.814842	0.310691
H	2.522689	–0.330276	0.428207
H	1.780236	–0.786678	–1.115066
O	0.568295	1.312650	–0.188471
H	–0.023545	1.909797	0.276765
O	–0.691534	–0.670533	–0.260021
H	0.254693	0.047003	1.404361
C	–1.952652	–0.130688	0.078213
H	–2.104128	0.860932	–0.360290
H	–2.081175	–0.064166	1.166544
H	–2.707925	–0.803314	–0.322246

E = –269.6791074
E[CCSD(T)/CBS] = –269.2957249
ZPVE = 0.1122370

Frequency	Intensity
113.9842	4.1829
191.1030	7.6228
212.7047	2.5786
279.4805	10.2074

292.0185	81.5400
391.7327	9.3512
522.9182	7.7126
573.3771	3.1647
846.5114	13.3961
910.0749	92.9995
1047.0316	52.2764
1086.6577	11.2655
1121.7567	114.7207
1138.3006	123.6245
1174.3659	3.8132
1218.9466	68.6896
1279.1040	51.9493
1382.7718	16.9443
1402.2539	3.4056
1451.9164	44.1758
1472.6888	2.6882
1485.2261	4.4089
1489.9935	3.0874
1493.1528	1.8223
1513.7728	5.5815
2936.8754	66.1257
2969.6491	70.6755
3024.1952	54.5055
3050.7077	9.6589
3112.0526	23.4172
3122.3210	18.0162
3127.1793	17.1993
3831.3310	24.6281

1c-d_8

Frequency	Intensity
95.8160	2.1758
143.7275	4.2946
156.3754	4.4323
210.8215	41.0665
248.0821	10.1252
340.2033	3.0345
452.8341	5.1994
538.7269	5.3499
708.0674	3.3873
772.4999	37.5428
829.3622	11.2548
877.2430	4.2055
909.6745	11.8134
936.7464	4.8835

1011.5911	41.0047
1033.0601	14.0442
1065.4167	30.9767
1068.5744	31.1552
1076.4114	3.3158
1085.7264	36.6794
1092.5225	2.0599
1097.4726	31.4962
1129.1039	172.1395
1160.4539	31.5163
1290.6574	79.7754
2132.9388	36.1904
2162.7022	55.0151
2191.6732	3.2114
2240.0705	33.1398
2303.7193	14.7623
2313.4736	8.5670
2318.1657	8.0619
2789.4659	17.0849

1c^{+}

C	1.569632	–0.613545	–0.149477
C	0.333768	0.025447	0.633195
H	1.647884	–1.660415	0.125851
H	2.457460	–0.066751	0.158650
H	1.372784	–0.491586	–1.211738
O	0.098849	1.330467	0.347039
H	0.859951	1.893459	0.550679
O	–0.756751	–0.758342	0.405380
H	0.600351	–0.149265	1.702776
C	–1.952728	–0.195887	–0.145648
H	–1.721820	0.268322	–1.110361
H	–2.315109	0.593777	0.520761
H	–2.652495	–1.016689	–0.238257

E = –269.3387711
E[CCSD(T)/CBS] = –268.9352339
ZPVE = 0.1091750

Frequency	Intensity
110.5015	8.1210
156.9752	1.4252
239.2617	1.2685
286.9879	15.5166
325.0052	86.5269

369.3747	26.3233
458.2807	36.3359
624.1289	7.5646
724.9052	81.8222
851.7991	83.7811
891.2320	30.0141
985.2395	13.2086
990.7251	9.2721
1080.5598	1.8373
1116.1992	45.0240
1189.6306	41.2657
1202.0043	106.9119
1224.1111	101.0830
1315.1692	7.1584
1373.1033	7.1002
1407.3974	46.8047
1435.2851	27.2667
1452.9384	16.2519
1470.3271	0.9372
1472.0346	14.5979
2772.2575	69.4118
2993.8279	65.9888
3045.1534	2.4210
3061.3553	2.3405
3162.9986	0.2545
3179.8825	1.7048
3197.0212	8.6355
3756.6631	303.1346

1d

C	1.327187	–0.860470	–0.408246
C	0.508469	0.069260	0.468073
H	2.380974	–0.597059	–0.331453
H	1.034092	–0.771920	–1.453493
H	1.196529	–1.892186	–0.084154
O	0.651495	1.373361	–0.061778
H	0.203392	1.983135	0.534010
O	–0.850616	–0.294992	0.604716
H	0.875198	0.036179	1.497997
C	–1.597559	–0.407469	–0.600306
H	–1.467701	0.470043	–1.236848
H	–2.642428	–0.484059	–0.307112
H	–1.327108	–1.303970	–1.165174

E = –269.6790369
E[CCSD(T)/CBS] = –269.2960108

ZPVE = 0.1127460

Frequency	Intensity
127.1942	4.5168
174.8104	1.7438
240.1150	3.4836
297.0313	2.7444
378.6190	91.2602
406.1282	11.3107
475.0742	36.2619
643.9788	7.0871
821.4752	15.5616
908.9175	66.0737
998.9467	56.2569
1058.6555	56.4679
1120.7460	79.7564
1162.1969	151.5826
1175.2642	3.8318
1216.0483	4.5555
1281.0169	67.2644
1396.8352	2.1599
1402.3373	4.7933
1447.1607	39.9308
1468.5084	3.5765
1485.6308	2.0107
1492.7767	6.6821
1504.7098	2.2325
1515.0044	7.9281
3006.4383	61.6384
3018.7409	36.4410
3047.8793	6.9386
3065.2312	40.6983
3111.9742	28.1279
3117.8961	17.2997
3120.3424	20.5159
3802.3069	28.3822

1d-d_8

Frequency	Intensity
101.9735	1.8045
133.0290	1.7929
181.4868	2.6723
259.7570	0.7034
279.2696	61.9132
355.3013	2.9819
420.9170	18.9719

571.1796	6.7500
708.5907	6.4377
770.7454	26.3780
826.6040	13.9565
869.7595	8.1459
911.2214	3.1646
933.3231	12.9996
986.5963	21.1839
1040.3064	20.1349
1067.8675	27.1808
1070.4380	23.4223
1081.8800	3.1632
1086.4752	17.2045
1093.5849	1.0222
1101.7751	63.7735
1120.2420	147.6512
1157.1330	42.8800
1265.1400	77.0105
2156.0978	33.2980
2189.4492	3.0640
2225.5059	33.5356
2272.1185	25.0996
2307.1361	15.5462
2309.9054	7.7750
2312.6879	9.8610
2767.4053	19.1277

1d^{+}

C	–1.366465	1.207812	0.026418
C	–0.397967	–0.032387	0.294671
H	–2.383862	0.824522	0.038429
H	–1.103133	1.614170	–0.947007
H	–1.220651	1.936427	0.817453
O	–0.452437	–1.004943	–0.649532
H	–1.340994	–1.379144	–0.739824
O	0.863785	0.450872	0.466969
H	–0.717002	–0.382326	1.305315
C	1.939712	–0.020349	–0.351930
H	2.038258	–1.103189	–0.222649
H	2.819836	0.519903	–0.027135
H	1.699658	0.164716	–1.404366

E = –269.3387711
E[CCSD(T)/CBS] = –268.9352342
ZPVE = 0.1091760

Frequency	Intensity

110.4643	8.1179
157.0850	1.4249
239.2821	1.2671
287.0444	15.4685
325.1809	86.3874
369.4858	26.5075
458.3517	36.2538
624.1086	7.5669
725.0316	81.7655
851.9728	83.8827
891.3091	30.0255
985.3010	13.2421
990.7195	9.2759
1080.6006	1.8553
1116.1923	44.9042
1189.5370	41.9517
1202.0068	106.2089
1224.0968	101.0249
1315.1562	7.1872
1373.1287	7.0938
1407.4001	46.7996
1435.3211	27.2922
1452.9492	16.2443
1470.3360	0.9259
1472.0273	14.6014
2772.0337	69.4209
2993.8173	65.9867
3045.1785	2.4268
3061.3612	2.3396
3163.0171	0.2542
3179.8391	1.7038
3196.9477	8.6320
3756.6100	303.1168

1e

C	1.314544	–0.925161	0.143266
C	0.356862	0.250943	0.274430
H	0.878544	–1.839691	0.546650
H	2.239223	–0.718276	0.680930
H	1.546238	–1.094641	–0.910237
O	0.915538	1.439895	–0.205954
H	1.110145	1.320987	–1.142684
O	–0.848146	0.013418	–0.437194
H	0.123188	0.445884	1.327439
C	–1.807880	–0.761053	0.252206
H	–1.476851	–1.793068	0.413540

H	–2.704855	–0.778991	–0.363310
H	–2.054690	–0.317594	1.224158

E = –269.6762414
E[CCSD(T)/CBS] = –269.2926981
ZPVE = 0.1120400

Frequency	Intensity
68.1433	2.6170
185.4027	1.4309
230.9550	34.1368
253.6802	60.8705
320.0520	13.5479
412.1106	2.8085
478.4663	30.8949
548.1702	1.8097
833.3364	13.9260
927.5232	40.5586
1060.4437	78.9972
1079.8721	9.6402
1119.8356	192.9289
1140.3732	148.2043
1177.5777	3.6254
1214.4389	29.7381
1333.0799	6.4252
1376.3457	18.1569
1405.7222	25.3047
1425.7850	67.8672
1476.1702	1.1064
1483.8961	0.8941
1489.8544	7.7953
1500.4723	7.2710
1510.8184	6.8026
2976.1095	47.3921
2998.6236	52.0847
3019.4179	47.8910
3030.1041	20.3147
3095.3117	30.9557
3109.1514	44.8326
3109.7015	4.4725
3788.8382	27.2050

1e-d_8

Frequency	Intensity
57.2335	1.6965
140.7479	1.6243

168.5429	14.1220
183.2063	41.0819
276.9561	3.5583
362.2998	0.7486
432.8830	19.1115
488.3039	5.9358
703.5895	3.0948
762.1342	7.5093
864.1118	26.3963
879.0094	25.2219
912.3065	4.0416
952.9939	35.4927
993.9455	22.1184
1040.4334	2.7063
1065.6828	16.3848
1069.8385	4.9501
1078.7115	3.1554
1086.2557	3.4025
1090.4882	3.7224
1135.4769	211.2345
1154.2515	41.9941
1172.3478	61.2397
1225.3405	116.6520
2135.9105	36.7064
2176.8428	2.9775
2210.5343	32.5320
2239.2301	33.2733
2292.3108	14.1792
2302.1476	19.6586
2303.9890	7.9339
2757.0929	16.8265

1e^{+}

C	–0.878750	1.460966	0.058102
C	–0.458452	–0.186768	0.265683
H	–0.050201	2.028858	0.467802
H	–1.799091	1.565430	0.621293
H	–1.007157	1.575847	–1.012889
O	–1.527836	–0.903464	–0.103445
H	–1.377475	–1.399852	–0.926957
O	0.649378	–0.438358	–0.433108
H	–0.337098	–0.190671	1.362958
C	1.934757	0.057401	0.021796
H	2.198331	0.915309	–0.595779
H	2.638124	–0.751464	–0.159767
H	1.900064	0.315455	1.077553

E = –269.3339565
E[CCSD(T)/CBS] = –268.9325891
ZPVE = 0.1092120

Frequency	Intensity
88.2444	3.4868
139.5601	1.3362
220.3853	0.0640
256.8740	9.2973
303.2836	112.4868
352.6525	35.2170
366.7032	5.3966
536.1148	34.6958
552.3974	20.9487
885.7589	9.2088
901.0055	40.8019
932.4480	78.5425
995.3582	18.1041
1124.5242	27.6011
1148.1977	8.4973
1179.1493	103.1312
1249.5873	79.2351
1302.2053	7.0975
1329.1510	7.3787
1346.8412	39.4514
1438.4723	13.1863
1444.5709	9.1487
1459.1273	13.4602
1470.5641	15.8753
1491.0879	52.2385
2914.7641	18.8761
3045.3566	11.5216
3070.1270	4.9389
3135.4657	2.0046
3157.3586	13.5216
3203.0310	0.6850
3208.9795	3.1327
3689.1543	268.2177

1f

C	1.349909	–0.848810	–0.393675
C	0.494793	0.077374	0.462002
H	1.280269	–1.872872	–0.028977
H	2.391097	–0.530493	–0.352743
H	1.032143	–0.836325	–1.438700
O	0.555819	1.413464	0.006766

H	0.614436	1.421178	–0.953557
O	–0.834823	–0.381448	0.618239
H	0.872326	0.100206	1.483606
C	–1.648374	–0.381170	–0.540552
H	–1.724758	0.617030	–0.980721
H	–2.639990	–0.692299	–0.219404
H	–1.296294	–1.085244	–1.301941

E = –269.6750403
E[CCSD(T)/CBS] = –269.2918705
ZPVE = 0.1124100

Frequency	Intensity
87.8113	2.7041
183.6234	6.8338
243.8844	4.9409
297.5491	19.9921
307.0787	72.4185
401.2408	3.1482
470.9207	8.7878
631.7143	5.6638
812.1377	9.3681
908.2047	75.1323
1013.8206	42.4615
1057.7560	63.9672
1115.0889	98.7587
1149.0696	167.9441
1173.8494	15.0712
1214.9953	22.9952
1298.6593	11.2350
1397.8974	3.2769
1414.6153	17.2072
1422.2146	62.3972
1469.1110	0.4501
1489.0858	4.1002
1494.2670	2.5010
1503.3793	1.6723
1512.2657	10.8052
2990.6282	48.9555
3030.4301	10.0944
3043.6047	53.2467
3072.4477	9.8273
3099.0706	45.5222
3111.4073	21.6343
3115.3025	16.7110
3809.3522	19.8022

1f-d_8

Frequency	Intensity
71.1320	1.4260
139.9346	4.1839
181.8423	3.8694
219.7859	45.4145
264.9183	4.2330
347.8438	2.9022
426.1768	8.5519
557.8019	6.0090
703.3648	5.7705
755.4994	5.8615
852.4157	51.6240
863.8965	7.7976
910.4477	2.9424
940.9212	41.6342
973.9581	3.7409
1059.7916	4.5787
1068.5719	26.1862
1071.3793	4.0149
1082.7564	6.0174
1087.6962	11.8211
1092.5297	8.7903
1103.5584	103.0466
1122.7659	102.2404
1166.9369	41.8482
1220.3544	113.0889
2146.2837	33.2315
2179.0249	3.7820
2255.5579	31.6624
2268.0350	11.5451
2291.7914	20.3313
2304.4325	14.7578
2309.0559	7.3754
2773.0956	12.8642

$1f^+$

C	1.391350	–1.242946	–0.139706
C	0.456464	0.015581	0.161442
H	1.285943	–1.953052	0.674240
H	2.412127	–0.873256	–0.198741
H	1.063083	–1.665556	–1.086104
O	0.463989	0.967644	–0.804871
H	1.349791	1.327487	–0.958405
O	–0.797835	–0.446819	0.421872
H	0.842346	0.381752	1.142610

C	–1.916908	0.021971	–0.338505
H	–1.993760	1.108507	–0.226903
H	–2.781604	–0.499404	0.051920
H	–1.745436	–0.188220	–1.399622

E = –269.3387711
E[CCSD(T)/CBS] = –268.9352343
ZPVE = 0.1091770

Frequency	Intensity
110.4851	8.1385
157.0907	1.4176
239.2526	1.2666
287.0212	15.4245
325.1972	86.3492
369.4219	26.5678
458.2382	36.3711
624.0609	7.6266
724.7770	81.6695
852.1724	83.7771
891.3299	30.2285
985.3182	13.2983
990.6877	9.2790
1080.6646	1.8590
1116.1636	44.8702
1189.5971	41.6952
1202.0588	106.4847
1224.1220	101.0950
1315.2716	7.1105
1373.0643	7.1144
1407.4897	46.7721
1435.3241	27.2945
1452.9332	16.2377
1470.3630	0.9246
1472.0098	14.5916
2771.8545	69.4012
2993.8131	65.9315
3045.1658	2.4338
3061.3676	2.3410
3163.0690	0.2550
3179.8924	1.7052
3197.0269	8.6262
3756.6846	303.0340

Table S7. Cartesian coordinates of structures in the dissociation pathways of 1-methoxyethanol cation (**1**$^{\cdot+}$). B3LYP/cc-pVTZ optimized Cartesian geometry, enthalpy, and Gibbs free energies (hartree) at CBS-QB3 level of theory.

1-methoxyethanol cation (**1**$^{\cdot+}$)			
C	1.665286	-0.700920	0.303618
C	0.480028	0.102516	-0.403889
H	2.584618	-0.144438	0.121590
H	1.722686	-1.693721	-0.137243
H	1.430958	-0.747816	1.366804
O	0.262321	1.344966	0.099256
H	1.044709	1.910618	0.020377
O	-0.640496	-0.675652	-0.349859
H	0.778576	0.106963	-1.480834
C	-1.842140	-0.175856	0.253655
H	-1.632489	0.105449	1.293627
H	-2.567674	-0.978397	0.176945
H	-2.155032	0.732385	-0.276744

Temperature = 151.000000 Pressure = 1.000000
E(ZPE) = 0.108208 E(Thermal) = 0.110499
E(SCF) = -267.746393 DE(MP2) = -0.938668
DE(CBS) = -0.095969 DE(MP34) = -0.057109
DE(CCSD) = -0.032560 DE(Int) = 0.030137
DE(Empirical) = -0.048189
CBS-QB3 (0 K) = -268.780545 CBS-QB3 Energy = -268.778254
CBS-QB3 Enthalpy = -268.777776 CBS-QB3 Free Energy = -268.793634

Transition state (**TS**)			
C	-1.838259	-0.871587	-0.310740
C	-0.303051	0.358158	0.538696
H	-1.757120	-1.728673	0.347493
H	-1.420860	-0.959407	-1.307426

H	-2.702624	-0.227172	-0.188921
O	-0.208159	1.375017	-0.286843
H	-0.910421	2.031624	-0.160111
O	0.680797	-0.470413	0.600954
H	-0.904126	0.426906	1.444906
C	1.779374	-0.411609	-0.376414
H	1.383223	-0.601331	-1.373453
H	2.455855	-1.198672	-0.062118
H	2.246580	0.570111	-0.322504

vi=-209.3049

Temperature = 151.000000 Pressure = 1.000000

E(ZPE) = 0.107241 E(Thermal) = 0.109731

E(SCF) = -267.752659 DE(MP2) = -0.946650

DE(CBS) = -0.094342 DE(MP34) = -0.050898

DE(CCSD) = -0.024124 DE(Int) = 0.030199

DE(Empirical) = -0.048273

CBS-QB3 (0 K) = -268.779507 CBS-QB3 Energy = -268.777018

CBS-QB3 Enthalpy = -268.776539 CBS-QB3 Free Energy = -268.792857

Complex (**3**)

C	2.430183	-0.710017	0.230401
C	0.019136	0.521939	-0.570934
H	2.240619	-1.59199 0	-0.368105
H	2.177029	-0.724023	1.283271
H	3.151304	0.016817	-0.123508
O	-0.110434	1.394655	0.369320
H	0.519493	2.131405	0.299407
O	-0.751163	-0.472886	-0.628963
H	0.708138	0.655542	-1.399718
C	-1.770885	-0.725995	0.420181

H	-1.256382	-0.885892	1.365497
H	-2.277074	-1.621284	0.077850
H	-2.440958	0.129708	0.464554

Temperature = 151.000000 Pressure = 1.000000
E(ZPE) = 0.105582 E(Thermal) = 0.108917
E(SCF) = -267.769733 DE(MP2) = -0.934561
DE(CBS) = -0.092298 DE(MP34) = -0.051780
DE(CCSD) = -0.023024 DE(Int) = 0.030003
DE(Empirical) = -0.048265
CBS-QB3 (0 K) = -268.784076 CBS-QB3 Energy = -268.780741
CBS-QB3 Enthalpy = -268.780263 CBS-QB3 Free Energy = -268.798523

CH_3 radical

C	0. 000000	0.000000	0.000000
H	0.000000	1.080506	0.000000
H	0.935745	-0.540253	0.000000
H	-0.935745	-0.540253	0.000000

Temperature = 151.000000 Pressure = 1.000000
E(ZPE) = 0.029274 E(Thermal) = 0.030728
E(SCF) = -39.576432 DE(MP2) = -0.153698
DE(CBS) = -0.015807 DE(MP34) = -0.021303
DE(CCSD) = -0.003287 DE(Int) = 0.005779
DE(Empirical) = -0.009324
CBS-QB3 (0 K) = -39.744799 CBS-QB3 Energy = -39.743345
CBS-QB3 Enthalpy = -39.742866 CBS-QB3 Free Energy = -39.752625

Fragment ion ($\mathbf{2}^+$)

C	-0.909628	0.013397	0.000000
O	-0.637556	-1.239456	0.000000

H	-1.422908	-1.814797	0.000000
O	0.00000 0	0.872348	0.000000
H	-1.934437	0.385908	0.000000
C	1.444927	0.497381	0. 000000
H	1.645073	-0.076102	0.902453
H	1.955852	1.453286	0.000000
H	1.645073	-0.076102	-0.902453

Temperature = 151.000000 Pressure = 1.000000

E(ZPE) = 0.073863 E(Thermal) = 0.075793

E(SCF) = -228.190522 DE(MP2) = -0.775818

DE(CBS) = -0.076144 DE(MP34) = -0.030745

DE(CCSD) = -0.019300 DE(Int) = 0.024159

DE(Empirical) = -0.039004

CBS-QB3 (0 K) = -229.033511 CBS-QB3 Energy = -229.031581

CBS-QB3 Enthalpy = -229.031103 CBS-QB3 Free Energy = -229.045597

Table S8. The ωB97X-D/6-311G(d,p) optimized geometries and harmonic frequencies of the reactants, transition states, intermediates, and products depicted in Figures 5 and S6.

R1			
C	-1.329779	-0.309798	0.306216
C	-1.415721	1.142755	-0.053559
O	-1.104293	-1.199617	-0.472110
H	-1.483523	-0.532620	1.383208
H	-0.598237	1.659164	0.458405
H	-2.355666	1.566897	0.311353
H	-1.330161	1.279247	-1.131484
C	1.931742	0.236727	-0.527190
O	1.510684	-0.101395	0.781464
H	2.139355	1.307760	-0.531496
H	1.155919	0.024122	-1.272694
H	2.850192	-0.290422	-0.812557
H	1.253543	-1.024156	0.767626

Frequencies		
63.7147	81.3862	105.6514
116.2358	149.9844	161.7214
178.5517	487.3129	516.8849
784.8979	903.4662	1081.0503
1111.1576	1139.6672	1144.7354
1190.9162	1375.4236	1399.3824
1437.4652	1466.5220	1475.5095
1496.0856	1501.2066	1526.8254
1852.0457	2912.7724	3010.7727
3045.8338	3070.4016	3122.4603
3127.6907	3161.5188	3916.9667

TS1

C	0.821763	-0.168981	-0.381147
C	1.067547	1.242303	0.077578
O	1.015664	-1.159247	0.441938
H	1.040426	-0.326048	-1.447631
H	0.597539	1.978504	-0.578411
H	2.149443	1.400711	0.048417
H	0.736918	1.375168	1.108184
C	-1.785737	0.336043	0.225550
O	-0.863574	-0.501822	-0.449825
H	-1.867622	1.288800	-0.302626
H	-1.484671	0.518204	1.263020
H	-2.760743	-0.154500	0.218482
H	-0.249445	-1.248471	0.221772

Frequencies

-1756.7334	109.1502	171.9935
210.0332	235.1665	369.1272
500.4511	508.2290	696.2759
910.6706	960.0773	1067.5703
1092.0966	1164.0080	1193.4032
1235.7242	1279.5662	1360.7920
1398.4265	1464.3470	1467.8494
1482.3619	1501.1209	1507.8575
1545.1542	2032.0097	3015.1173
3035.6478	3060.1678	3115.2148
3136.0848	3139.6794	3165.4872

P1

C	-0.552824	-0.119919	0.442263
C	-1.082780	1.163378	-0.167424
O	-0.899998	-1.165828	-0.430522

H	-0.998958	-0.278158	1.430954
H	-0.775467	2.019401	0.436382
H	-2.172284	1.125532	-0.205656
H	-0.713267	1.289583	-1.186987
C	1.662253	0.172907	-0.391703
O	0.826300	-0.108475	0.713577
H	1.653869	1.239467	-0.646448
H	1.370527	-0.409777	-1.271375
H	2.673708	-0.106022	-0.096849
H	-0.608439	-1.983797	-0.023269

Frequencies

138.2421	166.7575	251.1452
312.2554	392.8204	412.1547
488.5757	660.3627	845.4841
938.4233	1030.6731	1085.8634
1153.3113	1181.2918	1199.0773
1225.7504	1305.4469	1397.8221
1430.3292	1466.4659	1475.0610
1488.1526	1496.0628	1505.2752
1516.5601	3019.7788	3048.3558
3067.0945	3088.4660	3145.4951
3152.2779	3155.8175	3901.6918

R2

C	1.467904	-0.914024	-0.257103
C	2.769928	-0.253213	0.055740
O	0.711024	-1.354307	0.578629
H	1.217691	-0.989192	-1.330720
H	2.721804	0.765238	-0.339470
H	3.584744	-0.769896	-0.460114

H	2.947971	-0.239387	1.130494
C	-0.065395	1.919113	0.557094
O	0.096312	1.435740	-0.756948
H	0.723317	2.650476	0.745430
H	0.021602	1.117520	1.304709
H	-1.031720	2.420718	0.697616
H	-0.619303	0.797341	-0.904743
C	-2.817608	-0.494137	0.285419
O	-1.718506	-0.683143	-0.583477
H	-3.556054	0.107971	-0.245526
H	-2.532331	0.035270	1.203133
H	-3.283919	-1.447304	0.559700
H	-1.033410	-1.181512	-0.113050

Frequencies

40.7116	79.8489	85.2921
106.1497	112.2427	122.4045
138.6965	151.1289	162.5008
174.1485	197.3306	225.0528
236.8942	525.3713	657.9622
800.0673	847.3546	912.7017
1098.1664	1106.8361	1136.2659
1140.7794	1143.1899	1156.5354
1187.9937	1192.5748	1378.1383
1443.0918	1454.1900	1467.2272
1472.7176	1475.3875	1492.3758
1497.8810	1499.8418	1505.9542
1520.0115	1528.3262	1824.0633
2975.8768	2990.9073	3009.3358
3044.4439	3048.7077	3069.6030
3112.2511	3125.4396	3129.5728

3166.6546	3673.2365	3723.3579

TS2

C	1.087922	-0.682675	-0.290677
C	2.496828	-0.340142	0.109563
O	0.336628	-1.239069	0.598884
H	1.010242	-1.053913	-1.323458
H	2.970556	0.314947	-0.623469
H	3.062231	-1.273384	0.167033
H	2.511456	0.122142	1.097825
C	0.363609	1.750183	0.373748
O	0.342426	0.817602	-0.696450
H	1.324443	2.267745	0.390589
H	0.202079	1.241697	1.331220
H	-0.429369	2.484658	0.216128
H	-0.725517	0.339875	-0.722343
C	-2.709346	-0.072296	0.272836
O	-1.617619	-0.507041	-0.510692
H	-3.307551	0.641780	-0.299069
H	-2.381217	0.407924	1.203886
H	-3.344291	-0.924447	0.529675
H	-0.818622	-1.071384	0.105221

Frequencies

-1450.5867	67.1973	110.5955
131.8856	177.9587	210.9735
218.8128	241.8228	282.4647
336.3645	378.3028	475.6947
575.1472	616.5879	686.2285
932.8900	1011.1134	1053.2421
1089.0018	1149.5389	1155.5678

1187.8827	1194.6779	1202.8486
1237.3021	1295.6383	1349.8040
1353.3030	1401.8643	1472.5670
1482.4279	1493.9198	1500.3095
1506.6125	1514.8970	1519.3955
1535.7812	1558.9970	1593.4510
1755.7046	1950.1949	3009.1070
3017.3484	3032.8503	3065.3471
3089.2186	3113.4739	3116.3390
3136.8031	3145.5807	3162.6963

P2

C	1.098386	-0.536713	-0.329530
C	2.562977	-0.398606	0.028206
O	0.443083	-1.149211	0.734019
H	0.984016	-1.114869	-1.253616
H	3.090078	0.166267	-0.742955
H	3.007291	-1.391307	0.110496
H	2.679796	0.103012	0.990894
C	0.541477	1.705065	0.331445
O	0.484815	0.707955	-0.673799
H	1.535482	2.161701	0.385811
H	0.276951	1.292639	1.309880
H	-0.180388	2.473719	0.054336
H	-1.324567	0.038037	-0.890474
C	-2.845321	0.083230	0.316063
O	-1.988272	-0.595063	-0.581272
H	-3.394800	0.892787	-0.178678
H	-2.299170	0.499628	1.172625
H	-3.569219	-0.641492	0.690384
H	-0.467591	-1.307427	0.442608

Frequencies

51.1282	73.5291	103.6115
121.2530	148.3475	177.4800
196.1576	201.0103	266.2451
319.8241	421.2509	495.8251
633.6555	656.0264	782.7374
832.2638	940.6050	1039.1795
1090.6262	1108.9975	1137.1994
1162.2662	1185.0852	1186.0784
1187.5152	1230.1434	1358.5887
1404.5892	1422.4913	1458.8631
1474.0451	1484.7126	1490.9271
1496.1110	1501.1621	1508.9585
1519.8613	1520.6616	1525.4722
3003.6424	3026.7775	3050.4737
3062.0107	3062.9532	3097.8268
3130.6794	3138.4049	3146.8546
3150.9908	3706.2250	3745.6237

R3

C	-1.737740	0.766727	-0.355093
C	-3.122602	0.310035	-0.670348
O	-1.399671	1.210633	0.721885
H	-1.011587	0.717349	-1.186006
H	-3.062542	-0.728990	-1.000914
H	-3.524401	0.905808	-1.496028
H	-3.763507	0.400800	0.206016
C	-0.763308	-2.031078	1.072398
O	-0.866710	-1.771296	-0.308320
H	-1.748157	-2.335233	1.433183

H	-0.454111	-1.142502	1.640002
H	-0.057400	-2.844239	1.286102
H	0.024884	-1.527517	-0.616626
C	1.595300	2.712023	-0.039794
O	1.308251	1.462812	0.556826
H	1.014665	2.875020	-0.956287
H	2.655265	2.721916	-0.297059
H	1.399685	3.538507	0.651881
H	0.358558	1.437074	0.777173
C	2.699647	-1.597687	-0.214627
O	1.657396	-0.846331	-0.801798
H	2.706906	-2.583022	-0.683682
H	2.556622	-1.727264	0.865393
H	3.676871	-1.130082	-0.382949
H	1.606343	0.015711	-0.344168

Frequencies

11.8604	30.2866	44.2578
56.4348	69.4681	78.0247
95.8924	101.0220	106.3919
113.0035	122.1198	132.1011
135.9093	152.2461	172.2421
215.8484	249.1870	266.9392
294.0540	536.4371	780.5636
814.7429	836.3718	915.7933
945.8478	1098.6653	1105.4122
1111.8614	1139.8804	1141.5867
1148.2550	1154.8379	1164.8737
1188.1355	1188.9144	1189.1749
1375.4414	1439.3993	1463.4415
1471.1355	1479.3556	1480.8320

1486.3301	1490.2570	1496.3956
1499.2969	1501.0765	1501.9792
1505.8842	1520.5177	1525.6123
1535.3506	1812.3178	2978.2294
2992.9442	3006.5864	3010.5867
3046.4590	3049.2533	3065.8314
3074.2927	3111.4258	3122.8681
3130.1408	3130.7028	3168.9809
3516.0139	3603.1834	3616.9173

TS3

C	1.298412	-0.687904	-0.324992
C	2.788179	-0.846452	-0.511364
O	0.814061	-1.146583	0.783856
H	0.731225	-0.914467	-1.243340
H	3.145370	-0.290762	-1.379591
H	3.001779	-1.908454	-0.651341
H	3.313903	-0.516874	0.387039
C	1.458090	1.633478	0.761902
O	1.058717	0.949853	-0.419245
H	2.527324	1.848089	0.716070
H	1.236527	1.020847	1.640382
H	0.910048	2.576002	0.818168
H	-0.100302	1.054396	-0.558393
C	-2.092695	-2.161378	-0.136779
O	-1.568616	-1.048512	0.551302
H	-1.817705	-2.155616	-1.200628
H	-3.184113	-2.163467	-0.063775
H	-1.718273	-3.088653	0.307800
H	-0.442177	-1.164086	0.723815
C	-2.004943	2.112040	-0.076456

O	-1.323643	1.010382	-0.647821
H	-1.645548	3.034704	-0.538148
H	-1.848086	2.167964	1.007055
H	-3.076483	2.023576	-0.271062
H	-1.559898	0.056981	-0.112663

Frequencies

-1257.0361	41.3197	52.2013
75.1522	98.5514	102.7045
111.8360	142.1298	142.8320
162.7920	179.5582	202.9314
244.2485	286.3263	334.4321
386.5425	453.1526	549.5906
595.1896	642.4778	677.0852
936.9240	985.8087	1050.5279
1066.0151	1099.8831	1138.5627
1151.5453	1171.7457	1181.8803
1194.0250	1197.6596	1202.8278
1220.1042	1321.7970	1325.8197
1345.9859	1400.4185	1407.0773
1470.6677	1482.6559	1484.1877
1496.0817	1499.3877	1502.3474
1503.3989	1506.6679	1512.9115
1524.1978	1525.0644	1544.3726
1567.8923	1604.0676	1706.5559
1767.1654	1838.9679	2973.8490
3000.9350	3024.8394	3044.4753
3059.2522	3071.5013	3098.9578
3101.2345	3122.4612	3129.5374
3135.3073	3141.0579	3153.9053

P3

C	1.375272	-0.537903	-0.312707
C	2.854789	-0.746989	-0.564520
O	1.047093	-1.084866	0.909722
H	0.782176	-0.975438	-1.125387
H	3.165124	-0.229359	-1.474075
H	3.053927	-1.814070	-0.672245
H	3.441550	-0.381036	0.280603
C	1.600018	1.689707	0.584443
O	1.013668	0.851877	-0.397099
H	2.652694	1.890200	0.358807
H	1.516288	1.241749	1.577795
H	1.053600	2.633280	0.562104
H	-0.712758	1.094179	-0.681823
C	-2.024813	-2.332502	-0.259171
O	-1.651875	-1.292020	0.621085
H	-1.523295	-2.251038	-1.231982
H	-3.107656	-2.347951	-0.426510
H	-1.733677	-3.277972	0.200637
H	0.076024	-1.196077	0.939816
C	-2.114143	2.240503	0.048882
O	-1.687877	1.091468	-0.656291
H	-1.808655	3.159937	-0.463866
H	-1.726804	2.262093	1.075329
H	-3.203794	2.220064	0.092493
H	-1.839553	-0.437141	0.187404

Frequencies

19.9020	43.2449	51.5802
74.7118	93.6010	96.9272
111.7061	113.4777	125.2260

130.1646	179.1227	216.6414
228.4528	265.0507	272.0760
316.3411	433.1060	497.3519
653.3008	735.6663	817.6303
850.0073	937.9278	957.6662
1043.5449	1099.0114	1103.5701
1115.2135	1147.3098	1154.0376
1163.3845	1185.6922	1188.3396
1189.1205	1197.7523	1231.9234
1372.0569	1405.8792	1424.4526
1470.9085	1476.2776	1485.8845
1487.9900	1492.8547	1493.9934
1497.9616	1502.0293	1503.5646
1512.1390	1521.1766	1523.4703
1529.7079	1543.5172	3005.6090
3006.9955	3030.5565	3037.2288
3060.6742	3067.5750	3067.7619
3106.7822	3127.7606	3129.5897
3139.5799	3144.9418	3149.8269
3497.2420	3570.0722	3604.3580

R4

C	-1.726059	1.065462	-0.722331
C	-3.040535	0.923680	-1.413048
O	-1.588636	1.630574	0.345234
H	-0.847851	0.648624	-1.242341
H	-3.259505	-0.145714	-1.467063
H	-2.968857	1.306552	-2.435317
H	-3.822441	1.445624	-0.862084
C	-1.767434	-1.408857	1.394217
O	-1.781235	-1.532781	-0.009359

H	-2.704219	-0.937822	1.699444
H	-0.940971	-0.776946	1.745376
H	-1.697810	-2.385184	1.892242
H	-0.919319	-1.897444	-0.278461
C	1.523966	2.106698	1.997196
O	0.917978	1.109180	1.200387
H	1.525271	3.084000	1.500043
H	2.557276	1.806657	2.178075
H	1.019279	2.204376	2.964154
H	-0.008309	1.363854	1.007543
C	1.544589	-2.416891	0.628179
O	0.813809	-2.271045	-0.575253
H	1.101897	-3.241905	1.188967
H	1.500408	-1.509084	1.241821
H	2.595474	-2.662364	0.431228
H	1.138015	-1.460201	-1.004752
C	2.737478	0.786875	-1.844607
O	1.575141	0.242367	-1.258642
H	2.669379	1.877370	-1.935538
H	2.835518	0.365920	-2.846040
H	3.640964	0.536685	-1.275001
H	1.457322	0.608843	-0.358885

Frequencies

24.7947	27.0544	38.9914
40.5445	61.9153	71.4516
76.6823	82.5024	98.2806
101.2249	110.2960	114.5683
117.2178	118.8999	127.8746
142.9708	157.1729	159.7176
166.6850	175.1186	212.5057

237.8599	259.4503	271.2954
290.9847	539.0863	716.7214
766.7628	818.9118	887.2494
919.1441	943.7541	1092.7631
1102.6056	1108.6844	1116.6764
1139.4628	1147.2325	1150.4446
1154.4706	1157.7259	1172.8958
1185.7674	1187.4553	1188.3466
1194.9656	1375.0739	1458.4316
1463.9191	1470.8195	1479.4624
1480.1664	1486.9745	1488.7915
1490.7674	1492.2034	1496.4713
1500.9519	1502.3411	1502.7445
1503.1743	1511.4446	1527.9642
1531.1176	1535.8709	1548.7040
1800.8921	2995.3630	3005.8066
3007.6954	3014.3085	3015.4101
3048.9486	3051.8303	3066.7526
3068.6077	3079.5466	3112.3570
3122.5615	3126.6045	3128.9395
3129.4249	3165.1628	3468.5613
3540.9558	3601.4716	3656.2426

TS4

C	1.448409	-0.736393	-0.406552
C	2.696736	-1.513928	-0.787306
O	1.012403	-0.952686	0.816808
H	0.678575	-0.836532	-1.194086
H	3.102359	-1.187259	-1.747834
H	2.431394	-2.570963	-0.853486
H	3.456158	-1.413082	-0.008748

C	2.773865	1.254022	0.274861
O	1.780881	0.761580	-0.614735
H	3.771118	1.017478	-0.103240
H	2.635552	0.818121	1.268365
H	2.667315	2.339648	0.325677
H	0.648408	1.417539	-0.434226
C	-1.598410	-2.681098	0.464695
O	-1.356877	-1.315541	0.698114
H	-1.484414	-2.946440	-0.596571
H	-2.615957	-2.941940	0.774462
H	-0.898912	-3.295741	1.041708
H	-0.251988	-1.146462	0.801569
C	-0.440484	1.989122	1.228014
O	-0.307155	1.912268	-0.201698
H	0.170564	2.818160	1.584537
H	-0.117800	1.049764	1.681254
H	-1.486167	2.184134	1.465291
H	-1.111117	1.280079	-0.579309
C	-3.396330	0.801767	-0.700200
O	-2.055906	0.394449	-0.903503
H	-4.082064	0.096801	-1.178261
H	-3.539947	1.784771	-1.153508
H	-3.640037	0.860430	0.366968
H	-1.822527	-0.410021	-0.261516

Frequencies

-678.1938	23.1690	37.0644
44.7874	61.2696	73.5305
88.5544	92.0300	107.0619
120.3178	126.8032	133.3424
153.8814	177.9364	183.8485

197.9262	204.9759	260.7605
287.4363	334.6245	377.4668
469.3889	472.6808	514.3980
607.3498	678.2610	848.0911
948.1324	1011.3781	1051.3479
1070.0992	1095.1729	1117.6559
1137.7898	1141.7815	1164.7526
1172.0695	1186.5951	1189.9727
1192.2149	1198.2755	1222.6377
1256.7079	1307.3592	1318.4677
1380.5874	1401.4449	1406.3615
1424.1662	1453.0444	1467.5865
1474.2267	1481.4844	1484.3683
1489.7054	1494.2078	1500.4395
1503.6998	1503.8891	1510.5863
1513.0154	1515.2304	1523.2222
1526.3149	1554.3654	1589.4079
1627.5268	1706.0869	1813.4113
1926.9651	2284.3792	2938.5400
2989.1552	3024.4813	3039.1742
3052.2445	3055.1229	3060.5641
3085.9075	3094.1547	3122.4624
3123.3686	3129.1169	3138.6950
3140.1153	3155.0804	3161.2116

P4

C	-1.783534	0.565100	-0.475337
C	-3.114354	1.122564	-0.941305
O	-1.497163	1.057593	0.782458
H	-0.989478	0.812296	-1.189343
H	-3.420377	0.654816	-1.879080

H	-3.019657	2.198984	-1.091091
H	-3.884275	0.957548	-0.184590
C	-2.707369	-1.495172	0.371241
O	-1.777426	-0.870593	-0.497505
H	-3.725409	-1.437175	-0.027610
H	-2.673774	-1.042480	1.365769
H	-2.417787	-2.544568	0.436658
H	-0.210240	-1.626288	-0.429516
C	1.381268	2.816536	0.488876
O	1.171878	1.442365	0.745768
H	1.132528	3.081908	-0.545633
H	2.419168	3.107356	0.687139
H	0.730412	3.383759	1.155850
H	-0.525329	1.107897	0.873896
C	0.808313	-1.943019	1.195415
O	0.671383	-1.986918	-0.215567
H	0.022399	-2.524580	1.689659
H	0.784394	-0.917064	1.579475
H	1.771723	-2.389512	1.447872
H	1.840078	-0.899466	-0.876416
C	3.750772	-0.549477	-0.631895
O	2.449791	-0.143226	-1.007502
H	4.424950	0.292915	-0.794573
H	4.097287	-1.390653	-1.241818
H	3.802768	-0.836227	0.426169
H	1.682340	0.917560	0.093992

Frequencies

15.0911	29.3081	44.3664
51.4111	66.9951	75.2406
86.8889	89.9183	100.3040

103.8891	117.6794	126.4582
135.1125	142.7441	151.1098
188.1687	213.8107	226.5883
268.7440	297.1387	303.9055
319.7067	437.1875	496.6125
655.3365	816.3964	844.8192
874.0500	881.7324	911.6843
951.0184	1045.6688	1087.0466
1098.8469	1105.1026	1116.5720
1138.1816	1149.5895	1161.0012
1168.5680	1186.6398	1188.0224
1190.0643	1192.8295	1199.1987
1232.7365	1373.4601	1405.6187
1426.2811	1463.8480	1473.4169
1484.4751	1486.1855	1488.6319
1491.3846	1493.0122	1499.0228
1500.6078	1504.5027	1506.1009
1509.7836	1512.8349	1518.6956
1521.4630	1526.5548	1536.9503
1564.4903	3007.6374	3010.8473
3020.0165	3031.1152	3050.6894
3059.5677	3071.8385	3073.3324
3086.5179	3106.7323	3124.1202
3125.7028	3128.2486	3139.3226
3144.0211	3148.2161	3428.3938
3515.4070	3553.6973	3583.2952

R5

C	0.416982	-0.065779	1.631314
C	-0.011447	-1.009047	2.697898
O	0.947734	1.008970	1.832468

C	3.060167	-1.086717	-0.121060
O	2.184135	-1.988448	0.513157
H	0.214008	-0.391300	0.601353
H	0.590657	-1.914966	2.584979
H	-1.055343	-1.281934	2.520555
H	0.127892	-0.575664	3.687656
H	3.839468	-0.817378	0.594544
H	2.550267	-0.163781	-0.433384
H	3.544117	-1.528298	-1.002636
H	1.468057	-2.188566	-0.112907
C	1.915609	2.792780	-1.231867
O	0.931870	1.929397	-0.701021
H	1.943893	3.752114	-0.703216
H	1.666444	2.978615	-2.277185
H	2.909798	2.333940	-1.190026
H	1.122141	1.729053	0.237099
C	0.205705	-1.207549	-2.309315
O	0.033606	-2.123176	-1.242116
H	1.086732	-1.518446	-2.873541
H	0.368014	-0.184511	-1.948508
H	-0.655438	-1.215733	-2.987619
H	-0.784515	-1.871548	-0.775085
C	-2.072696	2.449740	0.591647
O	-1.731497	1.570621	-0.465802
H	-1.321034	2.436364	1.388158
H	-3.026501	2.117674	1.004965
H	-2.191422	3.476637	0.229641
H	-0.818378	1.772401	-0.741191
C	-3.464843	-1.400133	-0.456874
O	-2.166246	-1.042872	-0.026733
H	-3.590528	-2.470721	-0.289909

H	-3.614348	-1.193598	-1.523034
H	-4.235552	-0.869700	0.114045
H	-2.032112	-0.086353	-0.194834

Frequencies

31.6736	39.7464	46.1553
55.4389	59.3437	66.5351
71.6052	81.0624	89.4443
95.1870	102.3828	104.7566
114.7096	119.5797	131.3956
133.4453	140.7216	146.6928
151.0224	152.4882	156.8805
158.5640	170.9423	182.2671
188.7176	211.5681	227.3935
260.8274	284.3175	313.8222
319.1638	540.3146	767.6963
785.1497	842.7559	861.3960
887.5033	930.7852	933.1109
1089.2637	1093.6417	1103.9619
1110.4735	1112.9368	1138.8836
1144.8334	1156.2062	1157.8257
1164.7037	1172.5263	1178.2780
1188.2129	1191.2153	1191.5554
1194.8050	1196.4466	1384.2329
1452.8055	1462.3236	1469.0382
1472.7233	1475.5145	1485.2158
1487.2634	1488.6753	1493.5843
1494.6858	1497.0118	1503.3859
1503.6311	1507.4667	1508.6582
1509.7418	1510.0269	1512.6286
1525.3715	1528.3828	1531.0008

1534.6689	1549.9998	1806.9247
2997.5765	3016.7423	3018.9281
3022.6752	3027.8051	3047.8807
3059.8016	3079.4687	3079.5966
3082.3804	3085.8385	3094.2339
3121.6688	3125.4215	3131.3870
3135.6454	3137.1659	3142.7601
3171.9097	3464.2827	3530.6929
3595.5263	3618.0262	3664.0566

TS5

C	1.712629	-0.927347	-0.283444
C	2.828936	-1.841510	-0.734957
O	1.519564	-0.927761	1.033306
C	3.255111	1.040506	-0.160608
O	2.080401	0.495649	-0.762819
H	0.797620	-1.078864	-0.867742
H	3.061279	-1.695191	-1.791638
H	2.502348	-2.871379	-0.582292
H	3.724853	-1.685265	-0.130349
H	4.139885	0.661650	-0.673061
H	3.283341	0.776843	0.899326
H	3.206325	2.123288	-0.280952
H	1.164590	1.248600	-0.554425
C	-1.451480	-1.436782	2.287387
O	-0.876605	-0.642112	1.295905
H	-1.310163	-2.515511	2.103402
H	-2.536010	-1.261370	2.362380
H	-1.023638	-1.225228	3.279176
H	0.451611	-0.798895	1.223540
C	0.192881	2.257771	1.113832

O	0.343471	2.069082	-0.307378
H	1.191019	2.371390	1.536490
H	-0.305733	1.387288	1.547200
H	-0.371427	3.176274	1.279760
H	-0.566467	1.854726	-0.714851
C	-2.430688	-2.174096	-1.238918
O	-1.555171	-1.086172	-1.073555
H	-1.991207	-3.101090	-0.850721
H	-2.625467	-2.311678	-2.305197
H	-3.392017	-2.013122	-0.732127
H	-1.320786	-0.968831	-0.076887
C	-2.947857	1.637545	-0.201716
O	-1.954423	1.468259	-1.206753
H	-2.988592	2.697084	0.056851
H	-2.700875	1.048586	0.688192
H	-3.929536	1.337792	-0.580927
H	-1.876045	0.490812	-1.354236

Frequencies

-507.1544	33.1038	39.4006
57.1045	61.8967	75.9739
83.3013	90.6474	101.0073
117.9031	124.5330	130.4450
140.6153	158.2782	161.0859
163.4336	167.8851	181.3434
190.0091	199.1970	211.9441
231.2270	258.3745	276.7039
298.2157	322.5173	341.9513
377.7175	479.6210	494.2863
586.3709	661.4779	800.7789
938.4935	942.9608	1027.8591

1051.5236	1068.5919	1090.6282
1103.5017	1105.0764	1128.4053
1138.1902	1167.3448	1174.6252
1185.3771	1189.3388	1193.1081
1195.3630	1199.5602	1201.9967
1212.5222	1228.0747	1240.6222
1287.0970	1325.9828	1391.5820
1399.7056	1430.8808	1460.9340
1475.5818	1477.6788	1480.9016
1485.3840	1488.5428	1494.3057
1497.7776	1502.0186	1502.3475
1506.4952	1509.3835	1511.1127
1515.5325	1518.5120	1521.4759
1522.9955	1529.8282	1554.6367
1575.5542	1615.1484	1683.0605
1751.2070	1806.8303	2533.9486
2764.2376	2951.8532	2991.6502
3000.3424	3009.1699	3029.9867
3047.2571	3056.6381	3057.3809
3066.7234	3072.5952	3105.3228
3110.6880	3132.0690	3147.3178
3149.9184	3151.6182	3155.3170
3158.4385	3160.2475	3305.2743

P5

C	1.944587	-0.764997	-0.374106
C	3.091676	-1.571120	-0.950303
O	1.907938	-0.953937	0.998738
C	3.206435	1.285750	-0.218126
O	2.052991	0.625171	-0.709936
H	0.995834	-1.046830	-0.841864

H	3.219946	-1.348776	-2.011416
H	2.878477	-2.634327	-0.830820
H	4.020809	-1.354227	-0.418656
H	4.093393	1.030707	-0.807457
H	3.377574	1.037910	0.832952
H	3.017008	2.355483	-0.315291
H	0.667227	1.667657	-0.519894
C	-1.169823	-2.000375	2.251078
O	-0.792813	-0.858370	1.507441
H	-0.669325	-2.905826	1.887259
H	-2.254260	-2.157830	2.222800
H	-0.873603	-1.837392	3.288022
H	0.993050	-0.805965	1.297080
C	0.035198	2.406681	1.165374
O	-0.021034	2.303937	-0.248554
H	1.023936	2.743547	1.497753
H	-0.201160	1.454693	1.651480
H	-0.698751	3.154434	1.471452
H	-1.554583	1.822842	-0.880585
C	-2.409548	-2.074187	-1.562828
O	-1.479564	-1.127113	-1.080116
H	-2.022650	-3.069890	-1.339857
H	-2.537269	-1.988574	-2.647101
H	-3.391046	-1.966489	-1.084544
H	-1.076811	-0.991441	0.578748
C	-3.208097	1.391815	0.058059
O	-2.393627	1.365145	-1.101105
H	-3.440675	2.419623	0.357041
H	-2.732779	0.873689	0.900322
H	-4.145949	0.887097	-0.181893
H	-1.822083	-0.220166	-1.252152

Frequencies

26.2984	31.0684	37.2316
44.1285	51.8247	60.6379
71.2797	74.7097	85.6401
92.0651	102.5428	104.9408
116.5444	124.5860	126.3801
145.5905	149.9855	154.1650
161.6698	178.5686	197.1862
213.7258	215.7229	259.5993
280.2740	292.9606	309.4261
317.5814	434.5687	496.3983
652.7625	757.0692	807.4899
832.0583	851.7128	924.5965
945.5461	986.5583	1045.1966
1085.4958	1094.3332	1097.8996
1108.8132	1115.5501	1139.5402
1145.7270	1153.4423	1163.6957
1170.9097	1186.8059	1187.2382
1188.6658	1190.6548	1198.3965
1200.7406	1234.2035	1389.8001
1406.9878	1442.1203	1467.8141
1475.2942	1479.2690	1485.4409
1486.6838	1488.7029	1491.1285
1493.3632	1497.0086	1501.5162
1502.2650	1503.8074	1507.0575
1510.9836	1512.1784	1515.0595
1521.3294	1526.3439	1532.9279
1535.5564	1552.1798	1576.2023
3008.1038	3009.8586	3011.8876
3018.7160	3029.8238	3058.7378

3071.1718	3075.6239	3076.4406
3077.8052	3090.1354	3104.9903
3119.0073	3124.5015	3124.9056
3129.9871	3138.3392	3142.9813
3147.6949	3367.4523	3487.0144
3500.5886	3580.5408	3627.0914

R6

C	1.270110	-1.105336	-0.165067
C	2.720081	-0.783090	0.014341
O	0.510207	-1.359458	0.738308
H	0.904993	-1.097956	-1.209732
H	2.883119	0.221664	-0.384342
H	3.330038	-1.476841	-0.572260
H	2.999048	-0.829777	1.066781
C	0.487175	2.078804	0.625830
O	0.694134	1.630898	-0.693697
H	0.333801	1.246348	1.326667
H	-0.367276	2.764530	0.703029
H	1.381276	2.623693	0.934746
H	-0.120427	1.208146	-0.995193
C	-1.995505	-0.723612	-0.403990
C	-2.384444	-0.158032	0.924465
O	-1.489162	-0.095795	-1.303544
H	-2.217588	-1.798563	-0.545093
H	-3.433756	-0.389443	1.130455
H	-2.222229	0.919179	0.953295
H	-1.776935	-0.648541	1.689635

Frequencies

59.8219	72.1924	82.1952

94.3702	109.9562	114.6104
128.4035	134.0506	142.4336
161.3303	170.8098	182.6944
201.6687	224.6036	521.2365
523.0941	675.2135	789.1434
802.6298	908.2604	909.8652
1105.4991	1129.3331	1140.0812
1144.6272	1147.0378	1147.7151
1192.1705	1375.8147	1378.6871
1436.5803	1441.8762	1443.1051
1466.6346	1468.0554	1472.9210
1478.4906	1495.4677	1504.5673
1522.7265	1827.5380	1839.4550
2957.9503	2961.2188	2992.0502
3045.0497	3047.1463	3049.2996
3115.3222	3125.8744	3126.9908
3163.8142	3165.1619	3768.9790

TS6

C	1.032434	-0.683312	-0.376091
C	2.523434	-0.630978	-0.548753
O	0.597883	-1.243293	0.695405
H	0.468426	-0.854749	-1.301368
H	2.803280	0.019969	-1.376806
H	2.875693	-1.644869	-0.753281
H	2.994188	-0.290204	0.375073
C	0.800784	1.625278	0.934736
O	0.605724	1.008932	-0.334888
H	0.713724	0.876217	1.726871
H	0.038278	2.393708	1.068630
H	1.790143	2.082349	0.955282

H	-0.423875	1.006928	-0.574156
C	-2.246577	-0.260933	-0.446652
C	-1.956772	-0.748589	0.842178
O	-1.746077	0.758346	-0.983357
H	-2.915719	-0.865640	-1.081868
H	-2.587758	-1.557285	1.198793
H	-1.731557	0.011001	1.591442
H	-0.604882	-1.178100	0.721588

Frequencies

-1290.4314	84.4335	99.6898
125.6519	151.5355	175.8713
203.0938	231.8606	259.5717
296.5114	367.7785	389.1199
473.3475	555.8287	580.0965
593.9242	704.0864	898.8801
939.1599	1021.0718	1030.6941
1055.5288	1071.1702	1145.5191
1175.8763	1188.9663	1239.7813
1289.0632	1336.9089	1343.3864
1379.4489	1406.6226	1412.3238
1451.8962	1474.3877	1481.9308
1484.1910	1496.5713	1518.5183
1545.2227	1585.9981	1602.3218
1682.4389	2159.4493	2993.5338
3047.1009	3049.6365	3063.3827
3107.0976	3134.4549	3143.0145
3154.8857	3165.5788	3202.2843

P6

C	1.106573	-0.598750	-0.247239

C	2.612461	-0.704454	-0.354033
O	0.729127	-1.060356	1.010718
H	0.619355	-1.169752	-1.044413
H	2.955897	-0.261096	-1.290274
H	2.902525	-1.755485	-0.328452
H	3.094955	-0.200949	0.486090
C	1.103555	1.724613	0.401989
O	0.627776	0.726095	-0.485064
H	1.056394	1.379783	1.438646
H	0.454953	2.591465	0.276469
H	2.130735	2.013470	0.157876
H	-1.057247	0.520594	-1.059099
C	-2.532547	-0.329401	-0.204537
C	-2.303214	0.068291	1.049967
O	-1.861081	0.026483	-1.308418
H	-3.337632	-1.020345	-0.437411
H	-2.933042	-0.297601	1.849152
H	-1.539914	0.798270	1.294081
H	-0.234524	-1.097924	1.042561

Frequencies

60.3437	77.1655	95.9182
117.8711	143.0334	173.7296
197.1281	200.3482	259.9867
315.1310	423.5827	483.9444
524.3623	558.1543	661.4166
738.6269	826.5419	838.0761
853.4827	943.9361	983.2579
1035.0179	1046.9997	1098.2234
1159.4936	1184.4239	1187.8051
1206.1922	1231.0617	1330.3634

1350.7502	1402.7119	1425.0953
1431.9417	1470.0429	1475.2579
1482.6909	1490.6960	1499.5689
1510.5766	1523.4497	1712.1428
3033.5567	3062.9362	3066.5434
3107.4162	3144.9997	3148.3861
3153.0973	3167.5893	3185.7624
3266.2140	3587.4263	3793.6562

R7

C	0.693553	-1.584223	-0.857914
C	1.923365	-2.433800	-0.910524
O	-0.331616	-1.906931	-0.303839
H	0.761825	-0.606161	-1.370719
H	2.710667	-1.890042	-0.381971
H	2.242733	-2.565142	-1.948854
H	1.742950	-3.400507	-0.440766
C	1.363172	0.093599	2.051461
O	2.125756	0.182693	0.868653
H	1.820962	-0.667146	2.686922
H	0.324914	-0.203136	1.853955
H	1.352580	1.040207	2.608338
H	1.693990	0.838609	0.299042
C	-2.277802	0.052922	-0.187733
C	-3.286074	-0.922021	0.320781
O	-1.816927	0.955300	0.475895
H	-1.963941	-0.078273	-1.238356
H	-4.157264	-0.935235	-0.340850
H	-3.582273	-0.671874	1.338788
H	-2.830041	-1.914810	0.289724
C	0.632772	3.195770	-0.914554

O	0.508655	1.807329	-0.685519
H	0.600780	3.770596	0.018565
H	-0.153324	3.565696	-1.583177
H	1.598054	3.367552	-1.392505
H	-0.343476	1.629060	-0.248747

Frequencies

27.2893	32.3765	45.6924
51.1045	61.7026	63.5113
85.3807	93.3299	97.3328
102.2508	115.2157	125.5469
133.9614	142.9099	152.5661
165.6350	201.0238	221.2788
235.4797	266.0105	521.1688
533.7933	774.1620	799.8027
809.6880	820.0614	910.7194
917.7938	1102.0723	1107.2262
1136.3971	1141.0449	1145.6502
1149.6449	1151.9890	1157.8123
1187.1820	1188.1506	1373.9927
1380.6923	1439.6215	1449.1299
1456.5118	1466.8005	1467.4574
1476.7587	1480.6178	1483.0188
1494.7439	1497.0914	1501.8041
1503.7278	1520.6112	1529.0577
1819.6657	1829.9864	2965.5719
2982.4588	2996.7312	3010.9240
3046.7976	3051.0251	3052.9863
3071.0944	3114.1772	3128.2436
3129.4723	3129.6176	3163.7370
3168.9414	3601.7143	3689.5309

TS7

C	1.419529	0.701769	-0.502477
C	2.041827	2.009340	-0.887206
O	2.164864	-0.121420	0.147998
H	0.747972	0.258825	-1.248766
H	1.297256	2.704581	-1.274160
H	2.786373	1.813296	-1.663070
H	2.544162	2.447162	-0.024024
C	0.116823	0.627290	1.848611
O	0.147838	1.264786	0.560339
H	1.143263	0.538673	2.197734
H	-0.340090	-0.360747	1.761320
H	-0.451160	1.272529	2.519371
H	-0.734708	1.068140	0.084467
C	-0.160961	-2.168994	-0.525342
C	1.080857	-2.542536	-0.008307
O	-1.146894	-1.740831	0.127024
H	-0.241803	-2.171039	-1.632169
H	1.740246	-3.105453	-0.663439
H	1.120241	-2.797600	1.049312
H	1.731352	-1.153952	0.069880
C	-3.248970	0.926452	-0.243714
O	-1.946693	0.532671	-0.634073
H	-3.447395	0.689835	0.807803
H	-4.002613	0.432208	-0.863813
H	-3.336394	2.004860	-0.386100
H	-1.804260	-0.442881	-0.434040

Frequencies

-625.7765 36.8753 54.7354

88.6499	95.0992	108.6567
125.9575	130.4506	144.5156
161.0286	189.1621	226.1114
240.8949	260.5357	299.2046
319.9394	352.3724	429.9113
446.5797	555.0189	579.0741
655.4582	707.4759	936.7329
981.1573	995.4255	1025.4834
1031.5711	1046.7268	1090.6325
1104.6481	1151.0542	1163.3447
1186.2593	1192.4948	1202.5226
1257.3988	1289.7148	1311.1505
1323.2001	1357.9491	1403.4550
1413.0506	1463.0448	1472.3777
1477.2329	1483.7629	1488.4425
1501.3219	1503.2774	1511.4654
1524.8621	1544.1727	1564.7959
1587.7502	1613.3455	1732.4559
2686.7129	2908.0666	2999.9004
3052.8073	3054.6538	3065.0036
3066.6792	3093.6537	3114.2944
3130.0207	3147.1567	3156.0020
3168.4866	3183.1852	3207.4370

P7

C	-1.698082	-0.301453	-0.538362
C	-2.923497	-1.192162	-0.539658
O	-2.029311	0.888392	0.084844
H	-1.336469	-0.138128	-1.560902
H	-2.678073	-2.172350	-0.951925
H	-3.707224	-0.733490	-1.144100

H	-3.306728	-1.311977	0.475841
C	-0.662558	-1.121347	1.488381
O	-0.577389	-0.939713	0.083435
H	-1.339921	-1.943069	1.744116
H	-0.990955	-0.203386	1.977823
H	0.343309	-1.366830	1.829251
H	1.076120	-1.043419	-0.471428
C	1.074551	2.008824	-0.307749
C	0.284417	3.080232	-0.211207
O	1.635639	1.402967	0.746588
H	1.299770	1.561494	-1.275493
H	-0.099482	3.547832	-1.107657
H	0.075191	3.535518	0.749689
H	-1.301824	1.519007	-0.030943
C	2.708244	-2.136888	-0.349852
O	2.038621	-0.908068	-0.540790
H	2.494768	-2.575087	0.633044
H	3.779643	-1.945379	-0.416881
H	2.438443	-2.863673	-1.124176
H	2.014499	0.561078	0.431798

Frequencies

36.2397	42.2077	52.2154
65.3890	70.6253	84.8505
95.4354	111.4825	127.1572
139.6114	159.0925	172.2769
215.7961	246.2527	251.5308
319.2555	421.3286	481.1492
506.3989	615.2557	678.0308
713.2766	771.4466	821.3586
844.6869	919.5026	949.5613

989.7920	1033.0414	1037.2694
1099.4190	1110.0376	1148.8678
1156.9864	1185.5732	1188.1760
1196.1524	1222.8327	1232.6034
1334.8364	1347.0060	1400.5122
1420.9729	1433.8875	1454.5344
1472.3695	1478.3763	1480.7242
1486.4501	1494.5131	1498.0783
1503.2368	1510.2566	1519.7833
1521.9254	1746.4435	3009.5047
3034.5671	3039.9606	3061.7192
3071.3085	3120.4738	3133.3322
3141.6208	3145.8506	3151.4927
3152.0955	3170.1706	3268.8030
3560.0234	3624.4506	3696.6661

R8

C	2.066234	-1.112124	-0.346315
C	3.521942	-0.827411	-0.517356
O	1.638784	-2.087419	0.233835
H	1.369536	-0.374803	-0.783701
H	3.742240	0.060619	0.081298
H	3.741455	-0.593153	-1.562821
H	4.121147	-1.670728	-0.175304
C	0.858737	0.662113	2.209623
O	1.873769	1.132545	1.348602
H	1.339992	0.127848	3.030488
H	0.174914	-0.031838	1.703013
H	0.262370	1.481699	2.630540
H	1.433815	1.533892	0.583884
C	-2.605677	0.436762	-0.076633

C	-3.684638	-0.326104	0.613579
O	-2.052425	1.405065	0.395749
H	-2.317495	0.072777	-1.078845
H	-4.543975	-0.451487	-0.051246
H	-3.979799	0.172994	1.535781
H	-0.164412	-2.061164	0.289230
C	0.389666	3.052339	-1.601501
O	0.335653	1.857782	-0.848766
H	0.223506	3.938091	-0.977443
H	-0.346463	3.050640	-2.413956
H	1.385208	3.122773	-2.041884
H	-0.539625	1.788404	-0.425384
C	-1.252902	-2.500485	-1.244507
O	-1.100908	-1.960083	0.046497
H	-0.696238	-1.932382	-2.003397
H	-2.314899	-2.461440	-1.503439
H	-0.932910	-3.548031	-1.296004
H	-3.277519	-1.318365	0.830509

Frequencies

14.8547	22.9728	32.2227
39.5015	54.3892	56.5807
67.6317	68.7551	75.9318
80.0015	99.5629	106.1467
110.0522	115.8387	120.6206
132.9662	139.0931	139.7298
146.7757	159.8539	172.8963
200.7100	220.8510	245.3738
248.0248	276.8990	532.8638
534.8893	733.7907	794.3904
803.2923	820.8829	838.1829

921.3123	922.6192	1097.5095
1104.2559	1107.0587	1135.1857
1139.5854	1143.5974	1149.5876
1155.4171	1157.7065	1159.9935
1186.4075	1187.0133	1187.4431
1374.1243	1375.6341	1443.5364
1451.1567	1457.2992	1465.2506
1468.0819	1471.0514	1478.9999
1479.9941	1485.4899	1493.9413
1495.8590	1498.4895	1500.3288
1501.6605	1505.4691	1521.1369
1525.7539	1533.3840	1814.8422
1823.9799	2981.7490	2989.0555
2991.1484	3000.5215	3011.7884
3045.1514	3048.7209	3052.8404
3054.5300	3072.5605	3094.9782
3121.5063	3123.3812	3127.9235
3129.0614	3165.0506	3166.7417
3583.6625	3632.6200	3706.4318

TS8

C	0.062243	1.520046	-0.526157
C	-0.783672	2.541010	-1.205876
O	1.158318	1.859616	-0.008348
H	-0.060119	0.477026	-0.834459
H	-1.790119	2.157432	-1.369146
H	-0.325759	2.753487	-2.177586
H	-0.807543	3.458259	-0.618799
C	-0.565791	0.486907	2.039624
O	-1.184430	1.220911	0.984946
H	0.398794	0.955592	2.241788

H	-0.423620	-0.555966	1.744005
H	-1.182966	0.554777	2.938865
H	-1.872359	0.653082	0.551035
C	0.492795	-2.164130	-0.657847
C	1.682433	-2.467452	0.000219
O	-0.598658	-1.851729	-0.120688
H	0.552129	-2.119622	-1.765570
H	2.471523	-2.930123	-0.587060
H	1.616409	-2.764472	1.044984
H	1.857864	0.928115	0.226245
C	-3.865109	-1.000283	-0.191393
O	-2.649059	-0.350588	-0.502018
H	-3.785724	-1.594262	0.726287
H	-4.179260	-1.659373	-1.008039
H	-4.632485	-0.236944	-0.050858
H	-1.920388	-1.024225	-0.529859
C	3.796508	0.136266	-0.346821
O	2.605876	0.008153	0.418068
H	3.623696	-0.122645	-1.396863
H	4.564394	-0.522239	0.063166
H	4.141464	1.168999	-0.282807
H	2.181253	-0.981978	0.238500

Frequencies

-834.1617	11.2091	26.5211
44.2764	46.3948	52.2407
68.0618	97.9058	103.6560
112.7011	120.8998	132.3659
140.9247	154.4692	170.4799
182.3685	205.6956	212.2248
225.6542	243.1233	276.5774

305.1190	334.4258	391.7431
470.1303	525.2938	559.0728
670.6602	729.0587	793.8946
905.6591	937.7486	1014.3509
1027.3695	1037.8454	1056.7942
1079.1321	1093.4813	1120.3989
1144.2886	1165.3321	1173.0365
1174.0448	1177.2536	1186.8719
1198.2705	1205.5098	1211.6654
1259.5706	1386.8058	1397.6396
1405.8912	1427.9950	1435.3253
1469.5406	1473.5750	1480.6796
1485.1780	1490.6014	1496.5677
1499.1549	1500.8084	1508.5675
1511.2303	1516.0358	1534.3462
1553.2446	1570.0623	1627.3547
1674.3596	1740.0447	1862.0805
2903.7792	3015.3970	3036.5493
3039.1102	3056.7976	3081.0041
3100.8383	3115.1546	3115.9586
3123.6648	3126.2956	3141.6466
3143.6562	3146.0420	3182.4093
3202.0703	3207.0158	3327.2282

P8

C	-0.033142	-1.543365	-0.262047
C	0.569600	-2.296823	-1.423571
O	-1.126876	-2.219215	0.241964
H	-0.333431	-0.525363	-0.560655
H	1.438874	-1.765195	-1.815698
H	-0.172670	-2.401400	-2.215998

H	0.872433	-3.290148	-1.087665
C	0.576829	-0.822462	1.932631
O	1.007838	-1.409236	0.713989
H	-0.163247	-1.455771	2.425311
H	0.161805	0.178533	1.763693
H	1.458704	-0.737831	2.567514
H	2.097822	-0.246378	-0.016401
C	-0.309696	2.295855	-0.423432
C	-1.524507	2.819215	-0.237225
O	0.647565	2.305675	0.509679
H	-0.039943	1.824311	-1.368745
H	-2.238297	2.821850	-1.050111
H	-1.781234	3.320294	0.688921
H	-1.760292	-1.547318	0.544919
C	3.848784	0.585079	-0.413791
O	2.434157	0.571626	-0.432595
H	4.244477	0.562355	0.607879
H	4.177326	1.507436	-0.893588
H	4.259658	-0.261983	-0.973060
H	1.409263	1.776223	0.190674
C	-3.490293	-0.068841	-0.660857
O	-2.728421	-0.009700	0.532950
H	-2.854446	-0.017471	-1.553255
H	-4.230430	0.737075	-0.703500
H	-4.013610	-1.025058	-0.665516
H	-2.232315	0.820698	0.517140

Frequencies

17.4953	31.3124	42.9350
45.2494	61.4260	73.1414
93.5234	100.4490	104.1856

109.9756	118.7841	118.9200
134.5988	154.1521	158.2692
161.6882	192.0139	221.3693
228.9992	252.7028	280.5791
296.4516	402.4756	512.7451
524.4142	604.6170	613.9503
738.5208	788.2029	820.4030
842.4958	848.4217	945.3637
970.4614	992.8506	1025.8964
1083.6463	1087.1118	1106.7983
1109.1814	1120.3613	1141.3225
1161.2469	1187.6818	1188.0365
1191.6062	1205.4525	1226.1131
1232.4597	1340.3011	1375.3692
1405.7949	1420.0744	1422.4971
1436.1541	1466.6584	1472.0553
1483.2111	1489.7830	1492.2617
1493.4583	1498.5069	1499.7871
1500.3541	1503.6408	1515.7987
1518.2474	1525.1706	1529.5271
1742.6866	2983.2478	3013.4107
3018.9361	3028.7305	3060.6118
3078.7498	3084.0206	3116.0066
3134.0858	3135.7725	3140.8993
3147.2455	3149.4110	3152.3497
3167.6770	3266.2119	3450.3902
3550.6612	3649.8371	3740.5129

R9

C	0.806756	0.688024	1.474370
C	1.318139	-0.058133	2.660780

O	0.579161	1.876333	1.449443
H	0.640544	0.072181	0.573918
H	2.198271	-0.629187	2.354285
H	0.553150	-0.784260	2.953282
H	1.535995	0.615463	3.489083
H	1.760125	3.186991	-0.533319
C	2.505778	-1.172076	-1.226929
O	2.347541	-1.721698	0.059340
H	3.439173	-0.603898	-1.236418
H	1.684561	-0.490881	-1.492736
H	2.575330	-1.944851	-2.005357
H	1.467780	-2.129350	0.091085
C	-2.399071	0.335547	0.712534
C	-3.399646	0.137354	-0.378045
O	-1.804383	-0.557636	1.269279
H	-2.200948	1.382779	1.008217
H	-4.327014	0.663656	-0.134385
H	-3.593749	-0.922232	-0.542649
H	-2.985232	0.590116	-1.283470
C	-0.804315	-2.319795	-1.389460
O	-0.325915	-2.533223	-0.072393
H	-0.798827	-1.257570	-1.656550
H	-1.816424	-2.722984	-1.517248
H	-0.138947	-2.854831	-2.068592
H	-0.887697	-2.022345	0.524325
C	-0.055144	2.264754	-1.134560
C	1.339438	2.722544	-1.426777
O	-0.486929	1.169479	-1.409684
H	-0.715969	3.024268	-0.675623
H	1.302205	3.483178	-2.214321
H	1.960255	1.888404	-1.752883

Frequencies

39.9575	43.7315	50.9201
54.9958	63.4853	69.2053
75.8008	79.7794	84.5542
95.1084	102.4478	110.9666
119.3730	121.7968	125.8042
141.0839	143.8223	149.2856
160.6178	168.3738	179.4213
186.6411	204.5507	208.7515
227.4053	251.7828	260.6387
520.6825	521.9704	526.7112
639.9764	775.2192	791.3073
793.8028	815.9573	911.0053
913.3123	918.4653	1089.0010
1109.7960	1127.8490	1130.3588
1143.4336	1146.2473	1150.0320
1151.9810	1152.3095	1161.5127
1192.1880	1193.9137	1377.2462
1377.5607	1383.2630	1436.6867
1438.3441	1440.2133	1443.1636
1461.9358	1466.1777	1468.0949
1470.9506	1474.0492	1479.4100
1486.0468	1491.0065	1501.9742
1504.1695	1507.5053	1529.2565
1531.8775	1815.9899	1829.2709
1836.9523	2955.3788	2970.2102
2985.2311	3007.7377	3013.0219
3037.0925	3047.3849	3047.8459
3047.8894	3084.7151	3102.2164
3124.9398	3125.7809	3128.8619

3130.8670	3164.3804	3166.7099
3170.9213	3689.4526	3786.8310

TS9a

C	1.638635	-0.155992	0.939665
C	2.024506	-1.117799	2.021388
O	2.473238	0.800599	0.687188
H	0.580893	0.124886	0.924499
H	1.352090	-1.976060	2.046554
H	1.953806	-0.591709	2.976275
H	3.051965	-1.450775	1.873818
H	1.921309	1.609099	0.193339
C	1.874298	-0.569037	-1.680991
O	1.609884	-1.207562	-0.416522
H	2.791950	0.002521	-1.563869
H	1.043235	0.088221	-1.949167
H	2.022759	-1.360667	-2.415695
H	0.675241	-1.598924	-0.435493
C	-2.448806	0.470989	1.461953
C	-3.291588	0.669069	0.254728
O	-1.719046	-0.484475	1.633005
H	-2.462776	1.269920	2.226496
H	-4.090475	1.391030	0.423190
H	-3.694355	-0.284400	-0.093208
H	-2.600494	1.040529	-0.526561
C	-1.486339	-1.840762	-1.639897
O	-0.793527	-2.059906	-0.410749
H	-1.492538	-0.779081	-1.897724
H	-2.508444	-2.225578	-1.572554
H	-0.960411	-2.405443	-2.410655
H	-1.244696	-1.566444	0.299962

C	-0.220139	2.119076	-0.531830
C	1.060872	2.682145	-0.581069
O	-0.722937	1.264258	-1.291673
H	-0.828839	2.436889	0.352347
H	1.220555	3.578540	0.012559
H	1.579696	2.647992	-1.537791

Frequencies

-378.2774	40.8645	66.2385
69.9256	83.3132	89.5801
97.9609	103.3678	115.9668
133.6370	139.0611	158.7214
177.0249	187.1568	193.2983
202.5906	222.5343	229.7851
242.0431	256.8727	271.9843
278.9635	301.8495	351.4078
402.5008	471.9775	535.8519
550.1227	577.9901	690.6856
697.8324	763.3320	809.6143
932.4390	966.5644	999.3568
1024.3799	1036.7676	1045.0040
1068.5844	1108.9177	1123.4891
1133.4627	1149.6372	1153.7438
1198.7731	1200.0784	1205.2831
1232.0673	1251.7912	1291.0915
1338.4972	1387.0954	1396.8783
1411.4972	1430.3721	1438.5623
1468.6493	1469.1732	1470.8427
1474.5419	1478.3228	1483.5829
1486.8810	1494.9586	1503.7478
1512.7497	1531.0140	1544.5966

1545.9387	1633.4328	1645.0546
1789.9333	1806.2817	2802.4009
2863.2242	2917.6389	2967.9248
3038.2128	3051.6511	3065.0794
3095.7535	3100.8682	3111.1485
3120.6110	3146.2993	3147.8063
3152.7612	3163.5625	3167.1401
3186.9610	3201.4522	3580.6814

I1

C	1.540743	-0.284549	0.907247
C	1.782598	-1.275815	2.008266
O	2.487093	0.641096	0.793287
H	0.526956	0.119188	0.886965
H	1.048004	-2.081920	1.979620
H	1.688185	-0.753849	2.961931
H	2.789400	-1.686486	1.923043
C	1.891929	-0.517836	-1.640416
O	1.543437	-1.188902	-0.400767
H	2.860581	-0.050611	-1.489404
H	1.118739	0.218434	-1.876634
H	1.965295	-1.302030	-2.392719
H	0.576836	-1.565293	-0.484944
C	-2.448419	0.433693	1.438151
C	-3.217474	0.769972	0.215958
O	-1.770792	-0.568424	1.560650
H	-2.459712	1.166069	2.266159
H	-3.967258	1.540059	0.394707
H	-3.672092	-0.126557	-0.211329
H	2.068188	1.463437	0.375471
C	-1.452442	-1.692873	-1.787939

O	-0.810456	-1.991096	-0.543310
H	-1.407469	-0.621143	-1.992505
H	-2.488166	-2.041610	-1.763324
H	-0.922430	-2.247800	-2.562634
H	-1.281866	-1.527893	0.179727
C	-0.101711	2.174025	-0.431168
C	1.136457	2.777350	-0.509819
O	-0.589332	1.263737	-1.163779
H	-0.720785	2.502740	0.440080
H	1.338615	3.635514	0.121915
H	1.723737	2.675883	-1.419229
H	-2.454446	1.128779	-0.507225

Frequencies

32.9909	60.5426	68.8626
87.2135	90.1216	97.7108
100.5222	110.0255	127.7653
137.8145	161.9326	167.9243
185.0489	188.3601	197.0493
212.1385	218.5009	232.2423
237.9570	255.7290	282.3750
298.5853	324.2693	388.9147
486.1556	535.8176	537.6962
551.4995	608.0461	702.7296
733.2990	761.2306	837.9008
932.9966	972.4019	994.8843
1008.2423	1022.3079	1046.7277
1060.1134	1072.1747	1120.0045
1129.4187	1149.4537	1155.8311
1162.1134	1200.8204	1213.6475
1251.4980	1263.0123	1296.6691
1356.2236	1379.4204	1393.3952

1418.0020	1436.9886	1446.6299
1462.4626	1467.2096	1472.9578
1475.6942	1483.2877	1484.8746
1493.5411	1495.6828	1499.0561
1505.7977	1531.4895	1545.9320
1567.6714	1653.3784	1718.7691
1794.6865	2415.7471	2807.1476
2843.3151	2874.1257	2972.6345
3041.3441	3043.9018	3065.8470
3095.4145	3127.6464	3128.7521
3129.1847	3150.6164	3152.8018
3158.0970	3162.2914	3162.4068
3201.4269	3222.9509	3510.5974

TS9b

C	1.478666	0.565882	-0.769911
C	1.532310	1.661320	-1.804226
O	2.586078	-0.234048	-0.837530
H	0.563640	-0.029086	-0.850956
H	0.668157	2.322748	-1.718812
H	1.529673	1.213215	-2.798628
H	2.448799	2.239073	-1.673362
C	1.790856	0.463732	1.660314
O	1.392673	1.251730	0.531104
H	2.830222	0.160469	1.546444
H	1.142998	-0.411682	1.762784
H	1.698113	1.116473	2.529123
H	0.011183	1.616086	0.692228
C	-2.405367	-0.207846	-1.435463
C	-2.875139	-1.019235	-0.357499
O	-1.895301	0.921610	-1.321395

H	-2.409801	-0.634414	-2.449690
H	-3.464015	-1.879272	-0.666053
H	-3.341746	-0.453899	0.450725
H	2.316674	-1.130186	-0.552653
C	-1.519930	1.185913	2.001937
O	-1.019952	1.781095	0.785198
H	-1.283667	0.120883	2.019879
H	-2.595433	1.353798	2.029379
H	-1.054186	1.708486	2.835870
H	-1.495034	1.391923	-0.098382
C	0.123227	-2.362606	0.023905
C	1.378346	-2.838269	0.218816
O	-0.576975	-1.616786	0.818551
H	-0.352173	-2.608736	-0.945714
H	1.815203	-3.510415	-0.509707
H	1.876449	-2.721190	1.175770
H	-1.815050	-1.386432	0.187094

Frequencies

-643.7969	39.9366	71.6016
82.6166	95.0009	101.2893
113.7052	119.1266	138.6928
146.1435	168.1345	178.7404
188.1885	192.7611	203.1109
220.3656	237.3387	258.2734
278.2191	288.0371	309.5344
376.1080	406.1662	506.0767
524.4129	555.7834	600.1411
618.0715	705.5572	732.0596
766.2774	783.1687	816.2531
910.1940	945.9431	1020.2231

1028.3560	1032.5172	1045.1987
1058.3746	1072.8064	1083.0894
1093.9156	1126.8891	1167.4102
1191.3350	1196.0318	1217.1338
1227.3300	1239.6879	1283.3762
1350.2243	1360.1819	1370.9813
1406.0392	1410.5418	1415.6398
1427.4651	1454.4949	1459.8979
1480.3119	1485.3380	1488.5875
1492.3427	1496.0492	1506.1084
1512.1728	1521.2848	1532.4080
1546.0915	1565.4925	1671.3525
1734.7457	1829.4562	1928.2119
2350.9391	2934.4437	3032.0790
3048.9888	3065.2296	3069.0015
3085.2019	3103.9596	3143.3431
3149.0548	3152.5348	3157.3157
3165.9327	3173.4709	3176.5737
3191.1937	3244.6676	3516.8363

P9

C	-1.490272	-0.630951	-0.744855
C	-1.410948	-1.595849	-1.901286
O	-2.624049	0.161698	-0.869614
H	-0.591963	0.000068	-0.693838
H	-0.550059	-2.257896	-1.797093
H	-1.312440	-1.038988	-2.833312
H	-2.324564	-2.192352	-1.931592
C	-1.774678	-0.673151	1.626637
O	-1.524791	-1.422298	0.447937
H	-2.787125	-0.262644	1.615923

H	-1.048180	0.140481	1.740425
H	-1.681661	-1.366329	2.463013
H	0.185692	-1.933883	0.550511
C	2.514858	0.609178	-1.329754
C	3.113067	0.949597	-0.179260
O	1.808957	-0.486704	-1.588315
H	2.565757	1.264230	-2.196099
H	3.687881	1.864531	-0.129587
H	3.141300	0.280103	0.673537
H	-2.426543	1.024956	-0.488411
C	1.598461	-1.692105	1.885783
O	1.161640	-1.944766	0.563563
H	1.320087	-0.686485	2.223519
H	2.685994	-1.781955	1.899883
H	1.188206	-2.428112	2.584845
H	1.699994	-1.044234	-0.781959
C	-0.287332	2.513423	0.145110
C	-1.523594	2.933929	0.408881
O	0.473687	1.863173	1.044771
H	0.169036	2.669790	-0.831229
H	-2.074886	3.483526	-0.342029
H	-1.964218	2.798921	1.389591
H	1.316768	1.613020	0.629625

Frequencies

30.1921	41.2919	67.5057
71.8518	80.8001	86.3410
98.0763	103.9293	113.7103
125.9663	133.3823	136.1933
147.4630	167.8736	175.4573
181.6713	203.2648	212.5912

226.5072	253.1426	279.6915
296.4504	398.6912	504.3910
509.7066	534.6970	544.8351
601.4436	615.3766	747.8796
774.6991	787.5188	836.0829
843.6402	858.1533	918.7003
950.0195	985.7487	993.8528
1015.2575	1056.5504	1082.0510
1099.3319	1107.1715	1136.0336
1154.0845	1189.7600	1191.2478
1195.0562	1203.0211	1233.8122
1236.4903	1341.5802	1342.4313
1353.4503	1390.6855	1395.9272
1430.1512	1445.2683	1448.2460
1476.7423	1483.6461	1485.9048
1488.1000	1492.8690	1499.5212
1502.5662	1506.0256	1518.4888
1535.7431	1544.7123	1700.7191
1743.5478	3014.5563	3028.5842
3033.9059	3065.7728	3082.7026
3110.1444	3126.1422	3142.6825
3146.5982	3152.4930	3158.4269
3163.4657	3171.4764	3175.1001
3264.7881	3269.5955	3376.0953
3575.3702	3621.5158	3795.2645

Supplementary References

(1) Jones, B. M.; Kaiser, R. I. Application of reflectron time-of-flight mass spectroscopy in the analysis of astrophysically relevant ices exposed to ionization radiation: Methane (CH_4) and D4-methane (CD_4) as a case study. *J. Phys. Chem. Lett.* **2013**, *4*, 1965-1971.

(2) Turner, A. M.; Abplanalp, M. J.; Chen, S. Y.; Chen, Y. T.; Chang, A. H.; Kaiser, R. I. A photoionization mass spectroscopic study on the formation of phosphanes in low temperature phosphine ices. *Phys. Chem. Chem. Phys.* **2015**, *17*, 27281-27291.

(3) Hudson, R. L.; Coleman, F. M. Infrared intensities and molar refraction of amorphous dimethyl carbonate - Comparisons to four interstellar molecules. *Phys. Chem. Chem. Phys.* **2019**, *21*, 11284-11289.

(4) Bouilloud, M.; Fray, N.; Benilan, Y.; Cottin, H.; Gazeau, M. C.; Jolly, A. Bibliographic review and new measurements of the infrared band strengths of pure molecules at 25 K: H_2O, CO_2, CO, CH_4, NH_3, CH_3OH, HCOOH and H_2CO. *Mon. Not. R. Astron. Soc.* **2015**, *451*, 2145-2160.

(5) Hudson, R. L.; Loeffler, M. J.; Ferrante, R. F.; Gerakines, P. A.; Coleman, F. M. Testing densities and refractive indices of extraterrestrial ice components using molecular structures—Organic compounds and molar refractions. *Astrophys. J.* **2020**, *891*, 22.

(6) Hudgins, D. M.; Sandford, S. A.; Allamandola, L. J.; Tielens, A. G. Mid- and far-infrared spectroscopy of ices: Optical constants and integrated absorbances. *Astrophys. J. Suppl. Ser.* **1993**, *86*, 713-870.

(7) Kleimeier, N. F.; Eckhardt, A. K.; Kaiser, R. I. A mechanistic study on the formation of acetic acid (CH_3COOH) in polar interstellar analog ices exploiting photoionization reflectron time-of-flight mass spectrometry. *Astrophys. J.* **2020**, *901*, 84.

(8) M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, ; G. Scalmani, V. B., G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, ; J. Bloino, B. G. J., R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, ; J. L. Sonnenberg, W., F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, ; T. Henderson, D. R., V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, ; M. Hada, M. E., K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, ; O. Kitao, H. N., T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, ; M. J. Bearpark, J. J. H., E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, ; R. Kobayashi, J. N., K. Raghavachari, A. P. Rendell,

J. C. Burant, S. S. Iyengar, ; J. Tomasi, M. C., J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, ; et al. Gaussian 16 Rev. C.01. Gaussian, Inc. Wallingford, CT: **2016**.

(9) Becke, A. D. Density-functional exchange-energy: Approximation with correct asymptotic behavior. *Phys. Rev. A* **1988**, *38*, 3098-3100.

(10) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37*, 785-789.

(11) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648-5652.

(12) Dunning, T. H. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007-1023.

(13) Čížek, J. On the correlation problem in atomic and molecular systems. Calculation of wavefunction components in ursell-type expansion using quantum-field theoretical methods. *J. Chem. Phys.* **1966**, *45*, 4256-4266.

(14) Bartlett, R. J.; Watts, J. D.; Kucharski, S. A.; Noga, J. Non-iterative fifth-order triple and quadruple excitation energy corrections in correlated methods. *Chem. Phys. Lett.* **1990**, *165*, 513-522.

(15) Raghavachari, K. Electron correlation techniques in quantum chemistry: Recent advances. *Annu. Rev. Phys. Chem.* **1991**, *42*, 615-642.

(16) Stanton, J. F. Why CCSD(T) works: a different perspective. *Chem. Phys. Lett.* **1997**, *281*, 130-134.

(17) Peterson, K. A.; Woon, D. E.; Jr., T. H. D. Benchmark calculations with correlated molecular wave functions. IV. The classical barrier height of the $H+H_2 \rightarrow H_2+H$ reaction. *J. Chem. Phys.* **1994**, *100*, 7410-7415.

(18) Bergantini, A.; Abplanalp, M. J.; Pokhilko, P.; Krylov, A. I.; Shingledecker, C. N.; Herbst, E.; Kaiser, R. I. A combined experimental and theoretical study on the formation of interstellar propylene oxide (CH_3CHCH_2O)—A chiral molecule. *Astrophys. J.* **2018**, *860*, 108.

(19) Montgomery, J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. A complete basis set model chemistry. VII. Use of the minimum population localization method. *J. Chem. Phys.* **2000**, *112*, 6532-6542.

(20) Chai, J.-D.; Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615-6620.

(21) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B* **2009**, *113*, 6378-6396.

(22) Denney, D. J.; Cole, R. H. Dielectric properties of methanol and methanol-1-propanol solutions. *J. Chem. Phys.* **1955**, *23*, 1767-1772.

(23) Luna, R.; Molpeceres, G.; Ortigoso, J.; Satorre, M. A.; Domingo, M.; Maté, B. Densities, infrared band strengths, and optical constants of solid methanol. *Astron. Astrophys.* **2018**, *617*, A116.

(24) Bao, J. L.; Truhlar, D. G. Variational transition state theory: Theoretical framework and recent developments. *Chem. Soc. Rev.* **2017**, *46*, 7548-7596.

(25) Maity, S.; Kaiser, R. I.; Jones, B. M. Formation of complex organic molecules in methanol and methanol–carbon monoxide ices exposed to ionizing radiation – a combined FTIR and reflectron time-of-flight mass spectrometry study. *Phys. Chem. Chem. Phys.* **2015**, *17*, 3081-3114.

(26) Kleimeier, N. F.; Eckhardt, A. K.; Kaiser, R. I. Identification of Glycolaldehyde Enol (HOHC═CHOH) in Interstellar Analogue Ices. *J. Am. Chem. Soc.* **2021**, *143*, 14009-14018.

(27) Kleimeier, N. F.; Turner, A. M.; Fortenberry, R. C.; Kaiser, R. I. On the formation of the popcorn flavorant 2,3-Butanedione ($CH_3COCOCH_3$) in acetaldehyde-containing interstellar ices. *ChemPhysChem* **2020**, *21*, 1531-1540.

(28) Meadows, G. W.; Darwent, B. D. The reactions of acetaldehyde with methanol. *Can. J. Chem.* **1952**, *30*, 501-506.

(29) Dutta, P.; Dutta, M. A theoretical study of spectroscopic properties of a hemiacetal by TDDFT method. *Orient. J. Chem.* **2011**, *27*, 87-94.

(30) Zhu, C.; Kleimeier, N. F.; Turner, A. M.; Singh, S. K.; Fortenberry, R. C.; Kaiser, R. I. Synthesis of methanediol [$CH_2(OH)_2$]: The simplest geminal diol. *Proc. Natl. Acad. Sci. U.S.A.* **2022**, *119*, e2111938119.