Supporting Information for:

Rotational Spectrum of Laser-Ablated Mannitol: A Conformational and Photofragmentation Study

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Figure S01: LA-CP-FTMW spectrum of mannitol: (a) 2-8 GHz and (b) 6-12 GHz.

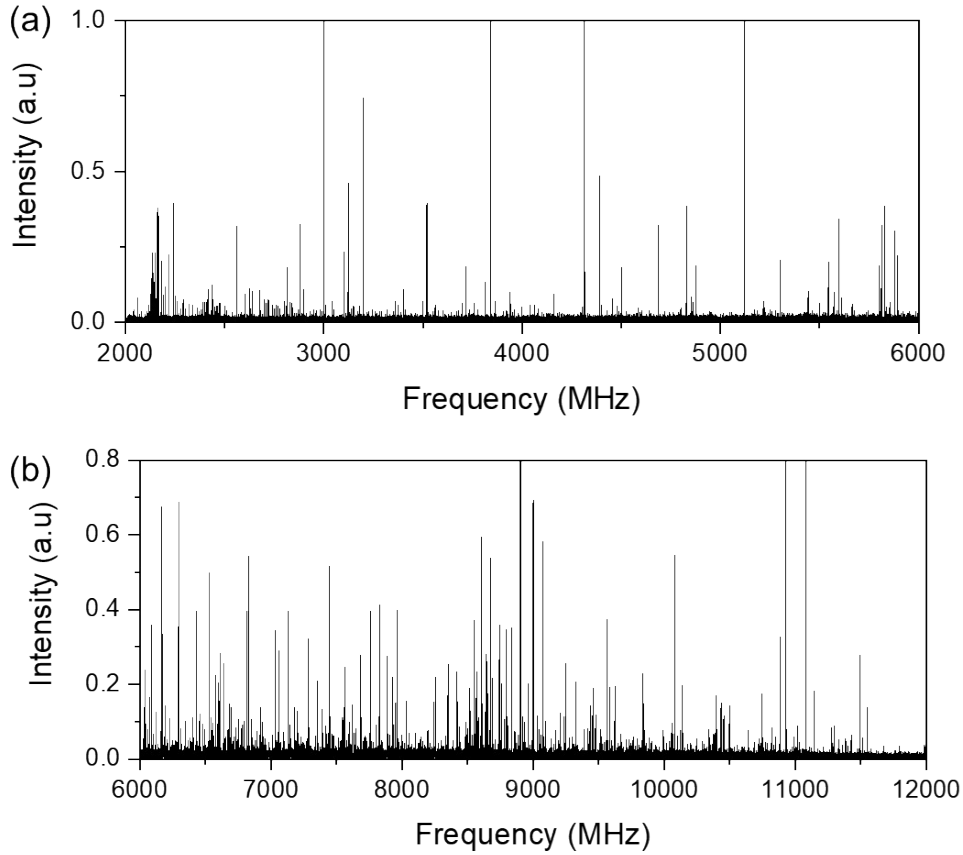

Table S01. Predicted parameters for mannitol conformers at different computational methodologies.

TG+T/G+G+/c	B3LYP-GD3BJ	MP2	B2PLYPD
A	1662	1679	1672
B	537	547	541
C	444	452	447
μ_a	-0.3	0.1	0.2
μ_b	-0.4	0.4	0.4
μ_c	0.3	0.3	0.3
ΔE	16	0	0
ΔE_{ZPE}	0	0	0
ΔG_{298K}	0	0	0

TG+T/G+T/c	B3LYP-GD3BJ	MP2	B2PLYPD
A	1668	1669	1670
B	517	524	519
C	418	424	420
μ_a	2.5	2.6	2.6
μ_b	0.2	-0.2	-0.2
μ_c	-0.9	0.9	0.9
ΔE	182	160	127
ΔE_{ZPE}	119	118	85
ΔG_{298K}	244	143	177

TG-T/TT/c	B3LYP-GD3BJ	MP2	B2PLYPD
A	1491	1477	1488
B	489	496	492
C	475	486	479
μ_a	0.0	0.0	0.0
μ_b	0.0	0.0	0.0
μ_c	-1.4	-1.4	-1.4
ΔE	575	640	561
ΔE_{ZPE}	330	367	315

TG+T/G+T/c´	B3LYP-GD3BJ	MP2	B2PLYPD
A	1670	1670	1672
B	514	521	516
C	416	422	418
μ_a	1.4	1.4	1.4
μ_b	0.3	-0.3	-0.3
μ_c	0.9	-0.9	-0.9
ΔE	199	290	191
ΔE_{ZPE}	163	239	161

ΔG_{298K}	356	291	309

TG-T/TT/c´	B3LYP-GD3BJ	MP2	B2PLYPD
A	1499	1483	1495
B	486	494	489
C	472	484	476
μ_a	1.7	1.8	1.8
μ_b	-0.7	-0.7	-0.7
μ_c	-2.4	-2.4	-2.4
ΔE	609	767	636
ΔE_{ZPE}	400	524	422
ΔG_{298K}	447	466	433

TTG-/G-T/c	B3LYP-GD3BJ	MP2	B2PLYPD
A	1484	1486	1487
B	524	529	526
C	458	465	461
μ_a	3.9	3.9	3.9
μ_b	-1.9	-2.0	-1.9
μ_c	-0.2	-0.2	-0.2
ΔE	406	445	406
ΔE_{ZPE}	363	427	385
ΔG_{298K}	518	498	517

G-TG-/TT/c	B3LYP-GD3BJ	MP2	B2PLYPD
A	1775	1780	1778
B	463	468	465
C	437	442	439
μ_a	0.0	0.0	0.0
μ_b	1.0	1.0	-1.0
μ_c	0.0	0.0	0.0
ΔE	196	431	316
ΔE_{ZPE}	163	395	291
ΔG_{298K}	360	478	449

G-TG-/G+T/c	B3LYP-GD3BJ	MP2	B2PLYPD
A	1565	1588	1573
B	529	533	530
C	497	504	499
μ_a	-2.0	-2.0	2.0
μ_b	0.9	0.7	-0.8
μ_c	-0.7	-0.7	-0.7
ΔE	303	539	418
ΔE_{ZPE}	246	442	356
ΔG_{298K}	456	518	519

TTG+/TG-/cc	B3LYP-GD3BJ	MP2	B2PLYPD

ΔG_{298K}	299	252	257

TG+T/G+G+/c	B3LYP-GD3BJ	MP2	B2PLYPD
A	1618	1637	1626
B	542	549	545
C	448	454	450
μ_a	-2.8	2.8	2.8
μ_b	0.5	-0.6	-0.5
μ_c	0.4	0.4	0.4
ΔE	295	306	266
ΔE_{ZPE}	265	281	250
ΔG_{298K}	395	288	343

TG-T/TG+/c	B3LYP-GD3BJ	MP2	B2PLYPD
A	1701	1690	1699
B	496	504	499
C	459	470	463
μ_a	2.1	2.2	2.1
μ_b	-0.7	-0.8	-0.7
μ_c	-0.3	-0.3	-0.3
ΔE	508	778	599
ΔE_{ZPE}	371	580	450
ΔG_{298K}	409	464	339

TG-T/TT/c´´	B3LYP-GD3BJ	MP2	B2PLYPD
A	1509	1491	1504
B	484	491	486
C	469	481	474
μ_a	0.0	0.0	0.0
μ_b	0.0	0.0	0.0
μ_c	-3.4	-3.4	-3.4
ΔE	661	915	729
ΔE_{ZPE}	487	696	545
ΔG_{298K}	552	652	573

TG-T/G+T/c	B3LYP-GD3BJ	MP2	B2PLYPD
A	1701	1689	1698
B	499	508	503
C	462	474	467
μ_a	-0.2	-0.2	-0.2
μ_b	0.5	0.5	0.5
μ_c	-1.6	-1.8	-1.7
ΔE	724	866	757
ΔE_{ZPE}	561	671	590
ΔG_{298K}	633	632	625

G-TG-/G+G+/c	B3LYP-GD3BJ	MP2	B2PLYPD

A	1626	1634	1630	A	1417	1445	1427
B	498	504	500	B	593	595	594
C	437	442	439	C	581	588	583
μ_a	0.5	-0.4	-0.5	μ_a	0.0	0.0	0.0
μ_b	-0.1	0.2	0.1	μ_b	0.2	0.1	-0.1
μ_c	0.3	0.3	0.3	μ_c	0.0	0.0	0.0
ΔE	877	1054	908	ΔE	393	671	517
ΔE_{ZPE}	664	811	693	ΔE_{ZPE}	336	528	439
ΔG_{298K}	763	773	744	ΔG_{298K}	576	630	631
G+G+T/TG+/c	B3LYP-GD3BJ	MP2	B2PLYPD	G-TG-/G-T/c	B3LYP-GD3BJ	MP2	B2PLYPD
A	1427	1423	1426	A	1407	1412	1409
B	551	562	555	B	564	573	567
C	453	461	456	C	488	495	490
μ_a	-0.3	0.1	0.2	μ_a	-2.4	2.5	2.5
μ_b	-0.3	-0.2	-0.3	μ_b	-0.5	0.6	0.6
μ_c	-0.4	0.4	0.4	μ_c	0.8	0.9	0.8
ΔE	838	786	808	ΔE	573	640	619
ΔE_{ZPE}	700	659	677	ΔE_{ZPE}	511	573	564
ΔG_{298K}	723	635	681	ΔG_{298K}	675	642	695
G+TG-/TT/cc	B3LYP-GD3BJ	MP2	B2PLYPD	TG+T/TG-/c	B3LYP-GD3BJ	MP2	B2PLYPD
A	1933	1944	1940	A	1731	1735	1735
B	457	461	458	B	501	507	503
C	419	423	420	C	403	409	405
μ_a	3.2	3.1	3.2	μ_a	-0.1	0.1	0.1
μ_b	-0.4	0.4	0.4	μ_b	0.1	-0.1	-0.1
μ_c	-0.6	0.6	0.6	μ_c	-0.3	-0.3	-0.2
ΔE	688	857	736	ΔE	869	1117	902
ΔE_{ZPE}	591	786	661	ΔE_{ZPE}	693	956	744
ΔG_{298K}	727	827	769	ΔG_{298K}	721	884	746
TG+T/G-T/c	B3LYP-GD3BJ	MP2	B2PLYPD	G+G+T/G-G+/c	B3LYP-GD3BJ	MP2	B2PLYPD
A	1731	1731	1733	A	1381	1394	1387
B	499	505	501	B	610	616	612
C	403	408	405	C	502	514	505
μ_a	-1.2	1.3	1.2	μ_a	-0.6	-0.8	0.6
μ_b	0.2	-0.3	-0.3	μ_b	-1.2	1.4	-1.2
μ_c	1.9	2.1	1.9	μ_c	1.8	-1.7	-1.8
ΔE	760	1097	833	ΔE	636	761	679
ΔE_{ZPE}	635	960	714	ΔE_{ZPE}	585	709	639
ΔG_{298K}	769	948	798	ΔG_{298K}	768	772	751
G-TG-/G+T/c	B3LYP-GD3BJ	MP2	B2PLYPD	G-TG-/TT/cc	B3LYP-GD3BJ	MP2	B2PLYPD
A	1699	1656	1683	A	1810	1824	1819
B	514	525	518	B	462	467	463

C	493	505	498	C	441	447	443
μ_a	-1.3	-1.7	1.5	μ_a	0.0	0.0	0.0
μ_b	-0.3	-0.4	0.4	μ_b	0.5	0.5	0.5
μ_c	-0.8	-0.5	-0.7	μ_c	0.0	0.0	0.0
ΔE	417	619	542	ΔE	128	488	309
ΔE_{ZPE}	420	516	515	ΔE_{ZPE}	200	572	398
ΔG_{298K}	657	511	680	ΔG_{298K}	449	731	619
G-TG-/G-T/cc	B3LYP-GD3BJ	MP2	B2PLYPD	G-TG+/TG-/cc	B3LYP-GD3BJ	MP2	B2PLYPD
A	1422	1434	1429	A	1501	1501	1503
B	564	571	566	B	518	524	520
C	493	501	496	C	477	483	479
μ_a	-2.7	2.7	2.8	μ_a	5.0	-4.9	-4.9
μ_b	-0.9	0.9	0.9	μ_b	1.6	-1.5	-1.6
μ_c	1.0	1.0	1.0	μ_c	-0.5	-0.5	-0.5
ΔE	269	453	369	ΔE	594	904	704
ΔE_{ZPE}	319	522	437	ΔE_{ZPE}	571	822	674
ΔG_{298K}	543	672	640	ΔG_{298K}	798	918	859
G+TG-/G-T/cc	B3LYP-GD3BJ	MP2	B2PLYPD	G+G+G-/G+G+/c	B3LYP-GD3BJ	MP2	B2PLYPD
A	1582	1589	1587	A	1313	1329	1319
B	528	533	530	B	682	688	684
C	459	464	461	C	507	513	509
μ_a	-1.7	-1.7	1.7	μ_a	-0.8	0.8	0.8
μ_b	2.3	2.3	-2.3	μ_b	-0.5	-0.6	-0.5
μ_c	0.5	0.5	0.5	μ_c	-1.3	1.4	1.4
ΔE	450	837	604	ΔE	0	404	170
ΔE_{ZPE}	456	826	618	ΔE_{ZPE}	220	593	392
ΔG_{298K}	704	949	827	ΔG_{298K}	618	795	725
TG-G-/TG+/c	B3LYP-GD3BJ	MP2	B2PLYPD	G+G+T/G+T/c	B3LYP-GD3BJ	MP2	B2PLYPD
A	1261	1254	1259	A	1508	1519	1512
B	647	659	651	B	525	532	528
C	585	593	587	C	464	468	465
μ_a	-2.8	-2.6	-2.7	μ_a	-1.3	1.4	1.4
μ_b	-0.3	-0.4	-0.4	μ_b	0.4	-0.4	-0.4
μ_c	-0.7	-0.8	-0.8	μ_c	1.5	1.5	1.5
ΔE	267	765	482	ΔE	810	931	829
ΔE_{ZPE}	333	737	522	ΔE_{ZPE}	686	807	714
ΔG_{298K}	690	908	817	ΔG_{298K}	797	817	793
G-TG-/G-T/c	B3LYP-GD3BJ	MP2	B2PLYPD	G+TG+/TG-/cc	B3LYP-GD3BJ	MP2	B2PLYPD
A	1401	1407	1404	A	1597	1604	1601
B	560	569	563	B	528	536	531
C	485	493	487	C	443	448	445
μ_a	-2.3	2.3	-2.3	μ_a	4.4	-4.3	-4.3

μ_b	0.2	-0.2	-0.2	μ_b	1.2	-1.1	-1.2
μ_c	-1.1	-1.0	1.0	μ_c	1.9	1.9	1.9
ΔE	649	840	749	ΔE	712	961	804
ΔE_{ZPE}	590	755	688	ΔE_{ZPE}	679	911	774
ΔG_{298K}	740	796	797	ΔG_{298K}	923	1048	982
G+TG-/G-T/c	B3LYP-GD3BJ	MP2	B2PLYPD	G+TG+/TG+/cc	B3LYP-GD3BJ	MP2	B2PLYPD
A	1571	1576	1574	A	1701	1720	1710
B	527	532	528	B	515	521	517
C	458	463	460	C	473	476	474
μ_a	-2.6	-2.6	-2.6	μ_a	-3.1	-3.1	-3.1
μ_b	-2.0	-2.1	-2.1	μ_b	0.6	0.6	0.6
μ_c	0.5	0.4	0.5	μ_c	0.2	0.2	0.2
ΔE	689	983	802	ΔE	612	880	718
ΔE_{ZPE}	633	948	764	ΔE_{ZPE}	604	831	707
ΔG_{298K}	825	1016	915	ΔG_{298K}	877	1001	947
G+TG-/G-G-/cc	B3LYP-GD3BJ	MP2	B2PLYPD	G-TG-/G-T/cc	B3LYP-GD3BJ	MP2	B2PLYPD
A	1302	1307	1305	A	1418	1431	1425
B	600	608	603	B	560	568	563
C	537	545	540	C	490	499	493
μ_a	-1.1	1.1	1.1	μ_a	-2.6	2.7	-2.7
μ_b	3.6	3.6	3.6	μ_b	-0.2	0.2	0.2
μ_c	-0.8	0.8	0.8	μ_c	-0.9	-0.9	0.9
ΔE	738	975	821	ΔE	379	680	528
ΔE_{ZPE}	696	918	788	ΔE_{ZPE}	428	719	583
ΔG_{298K}	908	1018	966	ΔG_{298K}	633	838	761
TTG-/TT/c	B3LYP-GD3BJ	MP2	B2PLYPD	TG-G-/TG+/c	B3LYP-GD3BJ	MP2	B2PLYPD
A	1860	1858	1862	A	1266	1258	1264
B	443	447	444	B	641	653	645
C	416	422	418	C	579	587	582
μ_a	2.0	1.9	2.0	μ_a	-1.1	-0.8	-1.0
μ_b	1.1	1.3	1.2	μ_b	-1.2	-1.2	-1.2
μ_c	0.9	0.9	0.9	μ_c	-1.9	-1.9	-1.9
ΔE	1159	1193	1158	ΔE	330	920	584
ΔE_{ZPE}	965	1010	976	ΔE_{ZPE}	417	899	639
ΔG_{298K}	985	951	968	ΔG_{298K}	778	1057	933
G+TG+/G-G+/cc	B3LYP-GD3BJ	MP2	B2PLYPD	G+G+T/G+G+/cc	B3LYP-GD3BJ	MP2	B2PLYPD
A	1419	1433	1425	A	1492	1499	1494
B	615	623	618	B	549	558	553
C	530	532	530	C	501	508	503
μ_a	-2.3	2.4	2.4	μ_a	0.9	-0.8	-0.9
μ_b	3.0	-3.1	-3.0	μ_b	-0.4	0.5	0.4
μ_c	-0.8	-0.7	-0.8	μ_c	0.5	0.5	0.5

ΔE	357	854	571	ΔE	686	848	760
ΔE_{ZPE}	448	853	639	ΔE_{ZPE}	658	809	736
ΔG_{298K}	844	1099	983	ΔG_{298K}	731	830	795
G-TG-/G+T/cc	B3LYP-GD3BJ	MP2	B2PLYPD	G+TG-/G-G+/cc	B3LYP-GD3BJ	MP2	B2PLYPD
A	1557	1583	1568	A	1389	1402	1395
B	533	536	534	B	623	630	625
C	502	508	504	C	515	521	517
μ_a	-1.9	-1.9	1.9	μ_a	-0.3	0.4	0.4
μ_b	0.6	0.6	-0.6	μ_b	1.5	1.4	1.4
μ_c	-1.0	-1.1	-1.0	μ_c	-0.1	0.0	0.0
ΔE	363	795	887	ΔE	758	1181	928
ΔE_{ZPE}	409	837	940	ΔE_{ZPE}	699	1083	866
ΔG_{298K}	666	1003	1165	ΔG_{298K}	904	1172	1036
G+TG+/G+G-/c	B3LYP-GD3BJ	MP2	B2PLYPD	G-G+T/G+G-/c	B3LYP-GD3BJ	MP2	B2PLYPD
A	1526	1535	1531	A	1240	1230	1236
B	547	553	549	B	690	707	696
C	497	502	499	C	523	537	528
μ_a	-3.0	-3.0	-3.0	μ_a	2.1	2.0	2.1
μ_b	-1.3	1.3	1.3	μ_b	-0.9	-1.0	-1.0
μ_c	-0.3	0.3	0.3	μ_c	1.7	1.8	1.7
ΔE	549	1073	756	ΔE	628	1003	765
ΔE_{ZPE}	592	1045	785	ΔE_{ZPE}	662	1043	815
ΔG_{298K}	852	1150	992	ΔG_{298K}	938	1181	1048
G+TG+/G+G-/c	B3LYP-GD3BJ	MP2	B2PLYPD	TG+G-/TG+/cc	B3LYP-GD3BJ	MP2	B2PLYPD
A	1531	1540	1537	A	1278	1286	1281
B	548	555	550	B	647	653	649
C	498	503	499	C	481	487	483
μ_a	-3.5	-3.5	-3.5	μ_a	2.5	2.4	2.4
μ_b	-1.9	1.9	1.9	μ_b	-0.8	-0.9	-0.9
μ_c	1.3	-1.4	-1.3	μ_c	-0.2	-0.1	-0.2
ΔE	610	1054	778	ΔE	597	1083	755
ΔE_{ZPE}	646	1041	810	ΔE_{ZPE}	657	1093	811
ΔG_{298K}	890	1140	1006	ΔG_{298K}	892	1192	1002
G+TG+/G-G+/c	B3LYP-GD3BJ	MP2	B2PLYPD	G-TG-/G+G+/cc	B3LYP-GD3BJ	MP2	B2PLYPD
A	1436	1452	1444	A	1386	1421	1400
B	616	624	619	B	605	606	605
C	521	525	522	C	584	592	587
μ_a	-1.6	1.5	1.5	μ_a	0.0	0.0	0.0
μ_b	-2.1	2.1	2.1	μ_b	-0.2	0.4	0.3
μ_c	0.6	0.4	0.5	μ_c	0.0	0.0	0.0
ΔE	657	972	808	ΔE	536	1028	768
ΔE_{ZPE}	613	947	786	ΔE_{ZPE}	574	1039	803

ΔG_{298K}	829	1134	1015
G-TG-/G+T/cc	B3LYP-GD3BJ	MP2	B2PLYPD
A	1747	1740	1747
B	510	515	512
C	485	493	487
μ_a	-1.0	-1.0	-1.0
μ_b	0.4	0.4	0.4
μ_c	-1.2	-1.2	-1.3
ΔE	292	987	605
ΔE_{ZPE}	461	1073	760
ΔG_{298K}	806	1266	1053

ΔG_{298K}	848	1220	1045
G-TG-/G+G-/cc	B3LYP-GD3BJ	MP2	B2PLYPD
A	1397	1390	1396
B	591	606	596
C	567	575	570
μ_a	2.1	-2.1	-2.1
μ_b	-1.3	1.4	1.4
μ_c	-2.1	-2.1	-2.1
ΔE	449	963	680
ΔE_{ZPE}	590	1021	805
ΔG_{298K}	908	1206	1078

G-TG-/G+G-/cc´	B3LYP-GD3BJ	MP2	B2PLYPD
A	1394	1388	1394
B	586	601	591
C	563	572	566
μ_a	1.7	-1.8	-1.8
μ_b	-1.4	1.4	1.4
μ_c	-0.1	-0.2	-0.1
ΔE	533	1159	812
ΔE_{ZPE}	677	1204	933
ΔG_{298K}	980	1367	1188

G-G-G-/TG+/c	B3LYP-GD3BJ	MP2	B2PLYPD
A	1206	1236	1214
B	700	696	699
C	656	650	655
μ_a	-2.2	-1.8	-2.1
μ_b	-1.1	1.1	1.1
μ_c	2.0	-2.2	-2.0
ΔE	424	1304	821
ΔE_{ZPE}	629	1383	991
ΔG_{298K}	1098	1581	1373

Table S02. Cartesian coordinates in Angstroms (Å) of detected conformers f mannitol at B2PLYP-GD3BJ/6-311++G (d,p) level of theory.

TG+T/G+T/c				TG+T/G+G+/c				TG-T/TT/c			
Atom	X	Y	Z	Atom	X	Y	Z	Atom	X	Y	Z
C	-1.496	-0.612	0.482	C	1.626	-0.131	-0.240	C	1.509	-0.031	-0.231
C	-0.761	0.583	-0.162	C	0.594	0.856	0.295	C	0.713	0.295	1.035
C	0.742	0.637	0.126	C	-0.849	0.580	-0.146	C	-0.713	-0.294	1.035
C	1.552	-0.478	-0.548	C	-1.492	-0.681	0.474	C	-1.509	0.031	-0.231
C	3.045	-0.181	-0.557	C	-3.005	-0.558	0.546	C	-2.964	-0.377	-0.103
O	3.537	-0.059	0.780	O	-3.560	-0.126	-0.700	O	-3.602	0.073	-1.307
O	1.316	-1.728	0.113	O	-1.219	-1.822	-0.334	O	-1.423	1.444	-0.458
O	1.275	1.872	-0.342	O	-1.561	1.771	0.217	O	-0.707	-1.699	1.252
O	-1.268	1.834	0.323	O	1.000	2.131	-0.189	O	0.707	1.699	1.252
O	-1.383	-1.767	-0.341	O	1.383	-1.417	0.341	O	1.423	-1.444	-0.458
C	-2.983	-0.330	0.640	C	3.041	0.307	0.101	C	2.964	0.377	-0.103
O	-3.556	0.191	-0.561	O	3.883	-0.787	-0.292	O	3.602	-0.073	-1.307
H	-1.084	-0.808	1.480	H	1.531	-0.196	-1.331	H	1.072	0.503	-1.083
H	-0.910	0.524	-1.246	H	0.629	0.840	1.394	H	1.226	-0.150	1.892
H	0.883	0.563	1.214	H	-0.866	0.463	-1.235	H	-1.226	0.150	1.892
H	1.211	-0.609	-1.578	H	-1.113	-0.834	1.492	H	-1.072	-0.503	-1.083
H	3.566	-1.030	-1.000	H	-3.419	-1.526	0.843	H	-3.038	-1.461	0.009
H	3.250	0.716	-1.141	H	-3.293	0.191	1.282	H	-3.404	0.116	0.771
H	3.362	0.842	1.070	H	-3.326	-0.789	-1.357	H	-4.550	-0.049	-1.222
H	1.865	-1.733	0.908	H	-0.272	-2.006	-0.232	H	-2.096	1.663	-1.113
H	0.597	2.535	-0.151	H	-2.399	1.745	-0.260	H	-0.050	-2.067	0.646
H	-2.134	1.958	-0.083	H	0.223	2.698	-0.101	H	0.050	2.068	0.645
H	-0.479	-2.100	-0.235	H	2.202	-1.917	0.224	H	2.096	-1.663	-1.113
H	-3.481	-1.255	0.943	H	3.291	1.220	-0.441	H	3.038	1.461	0.009
H	-3.148	0.425	1.406	H	3.119	0.484	1.180	H	3.404	-0.116	0.771
H	-3.456	-0.483	-1.242	H	4.778	-0.619	0.014	H	4.550	0.049	-1.222

Figure S02. 50 lowest-energy structures of mannitol.

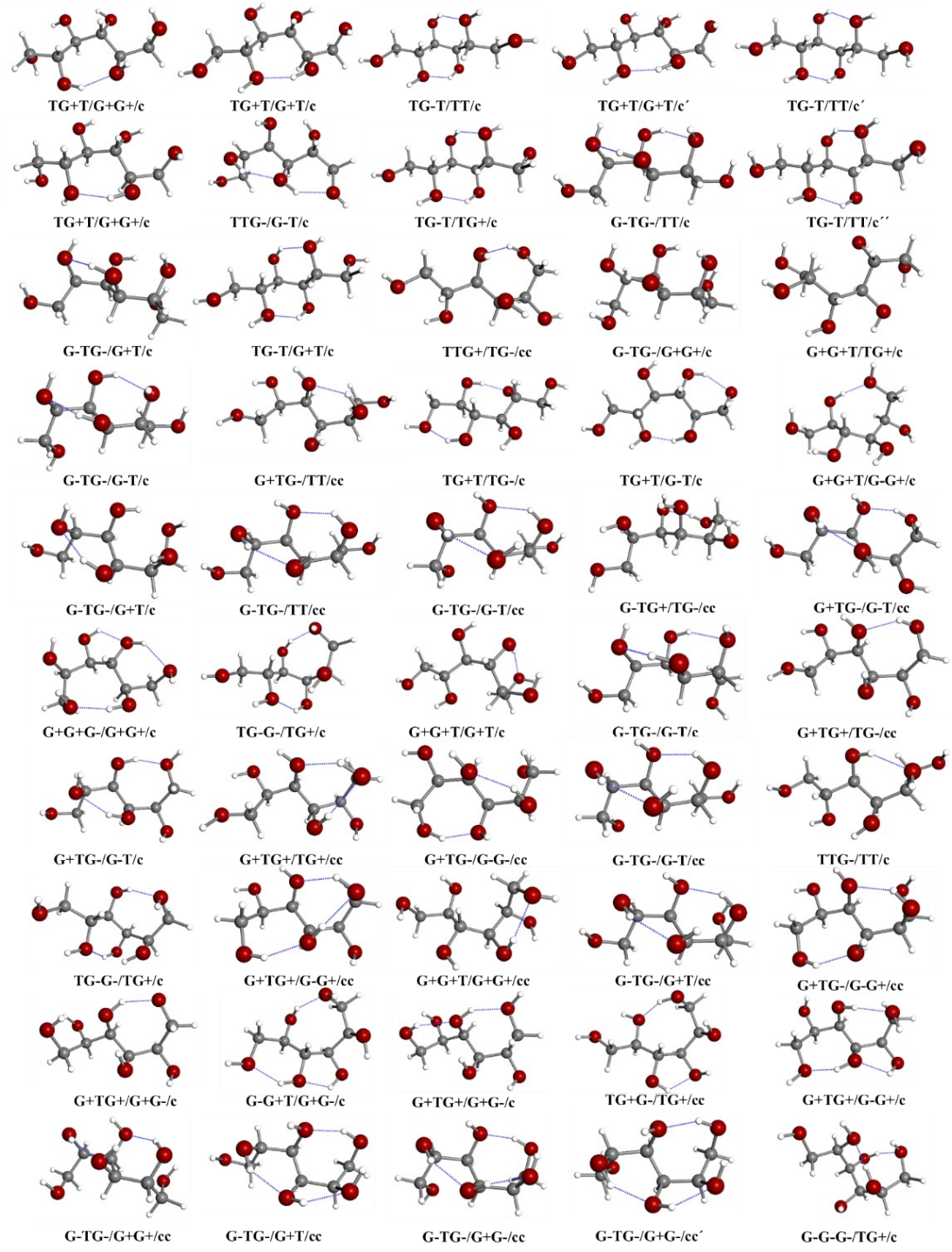

Figure S03. Summary of reaction network of fragment species of mannitol predicted by Automekin. Blue arrows represent barrierless processes, while black arrows indicate reactions with an energetic barrier.

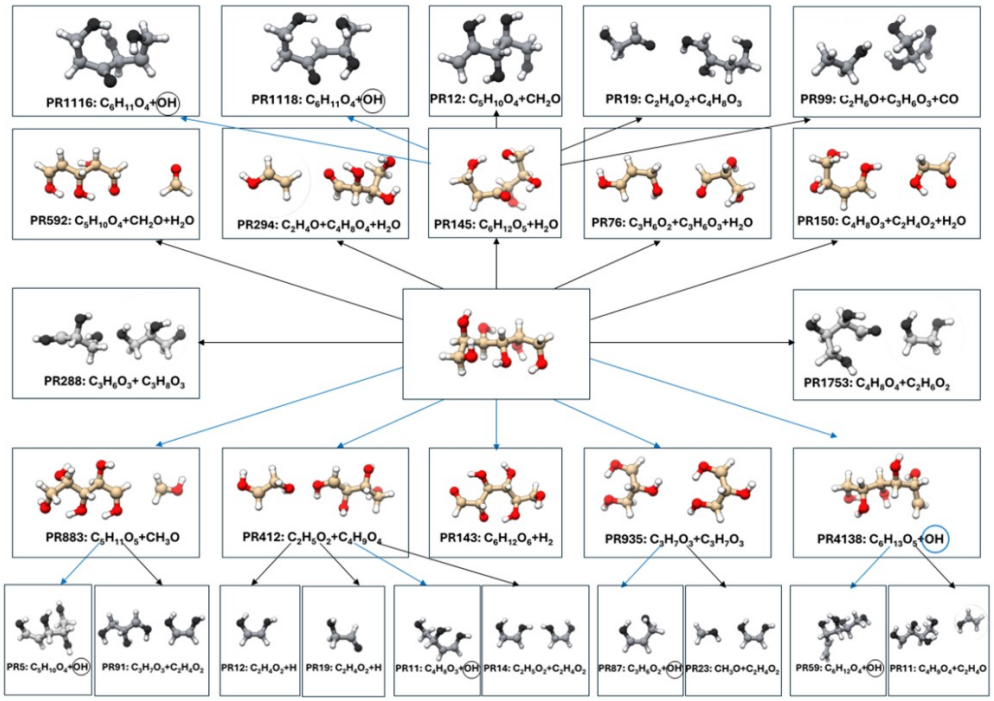

Table S03. Summary of known molecular species detected in the broadband spectrum of laser ablated mannitol.

Name	Formula	*N*[a]
Formaldehyde	COH_2	1
Hydroxy Radical	OH	2
Acetic Acid	$C_2O_2H_4$	4
Ethylene glycol (aGg' conformer)	$C_2O_2H_6$	5
Glycolic Acid	$C_2O_3H_4$	2
Syn-vinyl alcohol	C_2OH_4	1
Anti-vinyl alcohol	C_2OH_4	1
Acetaldehyde	C_2OH_4	7
Ethanol	C_2OH_6	1
Oxopropadienylidene	C_3O	1
Malonaldehyde	$C_3O_2H_4$	2
2-Hydroxypropenal	$C_3O_2H_4$	5
2-Hydroxypropanal	$C_3O_2H_6$	3
3-Hydroxypropanal	$C_3O_2H_6$	3
Glyceraldehyde (E conformers)	$C_3O_3H_5$	9
Glycolaldehyde	$C_3O_3H_6$	2
Glycerol (G'Gg'gg' conformer)	$C_3O_3H_8$	2
Glycerol (GGag'g' conformer)	$C_3O_3H_8$	4
Propynal	C_3OH_2	1
Trans-propenal/ Acrolein	C_3OH_4	1
Syn-Propanal	C_3OH_6	4
1-Butyne	C_4H_5	1
1,3-Pentadiyne	C_5H_4	2

[a]*N* represents the number of observed rotational transitions. [b]Species assigned with a single detected transition are classified as tentative. However, their assignment is robustly supported as the observed lines correspond to their most intense expected transitions under jet-cooled conditions, they are predicted as photofragments by AutoMeKin, and they are commonly observed ablation products in related molecules.

Table S04. Measured rotational transitions of Rotamer I (TG+T/G+G+/c).

J´	K´$_a$	K´$_c$	J´´	K´´$_a$	K´´$_c$	ν_{obs}	ν_{obs}-ν_{cal}
3	2	1	2	2	0	2843.245	-0.002
4	0	4	3	0	3	3699.351	-0.011
4	2	2	3	2	1	3813.510	0.034
4	1	3	3	1	2	3942.986	0.002
5	1	5	4	1	4	4427.928	0.031
5	0	5	4	0	4	4583.369	0.012
5	2	4	4	2	3	4684.998	0.013
5	2	3	4	2	2	4800.063	0.010
6	1	6	5	1	5	5300.138	0.014
6	0	6	5	0	5	5447.027	0.018
6	2	5	5	2	4	5610.922	0.014
6	3	4	5	3	3	5665.415	0.014
6	3	3	5	3	2	5678.317	-0.005
6	2	4	5	2	3	5801.828	0.016
6	1	5	5	1	4	5878.457	0.015
7	1	7	6	1	6	6166.833	0.014
7	1	7	6	1	6	6166.835	0.016
3	2	1	2	1	1	6292.131	0.037
7	0	7	6	0	6	6294.113	0.012
7	2	6	6	2	5	6530.938	0.015
3	2	2	2	1	2	6557.484	0.002
7	6	1	6	6	0	6594.944	0.019
7	6	2	6	6	1	6594.944	0.019
7	5	3	6	5	2	6599.508	0.019
7	5	2	6	5	1	6599.508	0.019
7	4	4	6	4	3	6607.811	0.021
7	4	3	6	4	2	6608.714	0.029
7	3	5	6	3	4	6614.766	0.014
7	3	4	6	3	3	6643.371	0.014
5	1	4	4	0	4	6678.142	0.023
7	2	5	6	2	4	6813.824	0.019
7	1	6	6	1	5	6827.997	0.014
8	1	8	7	1	7	7028.270	0.015
8	0	8	7	0	7	7130.652	0.009
4	2	2	3	1	2	7142.605	0.015
8	2	7	7	2	6	7444.233	0.010
8	7	1	7	7	0	7536.523	0.007
8	7	2	7	7	1	7536.523	0.007
8	6	3	7	6	2	7540.555	0.017
8	6	2	7	6	1	7540.555	0.017

8	5	4	7	5	3	7547.373	0.011
8	5	3	7	5	2	7547.373	0.011
8	4	5	7	4	4	7559.286	0.015
8	4	4	7	4	3	7561.728	0.016
8	3	6	7	3	5	7564.051	0.015
8	3	5	7	3	4	7619.816	0.016
4	2	3	3	1	3	7643.952	0.006
8	1	7	7	1	6	7760.775	0.010
8	2	6	7	2	5	7828.720	0.006
9	1	9	8	1	8	7884.990	0.015
9	0	9	8	0	8	7962.474	0.009
6	1	5	5	0	5	7973.226	0.022
5	2	3	4	1	3	7999.664	0.004
9	2	8	8	2	7	8350.165	0.005
9	7	2	8	7	1	8481.837	0.021
9	7	3	8	7	2	8481.837	0.021
9	6	4	8	6	3	8487.564	0.013
9	6	3	8	6	2	8487.564	0.013
9	5	5	8	5	4	8497.274	-0.016
9	5	4	8	5	3	8497.274	-0.016
9	3	7	8	3	6	8511.954	-0.003
9	4	6	8	4	5	8513.245	0.007
9	4	5	8	4	4	8519.057	0.023
9	3	6	8	3	5	8610.311	0.003
9	1	8	8	1	7	8673.336	0.004
10	1	10	9	1	9	8737.696	0.005
5	2	4	4	1	4	8778.669	-0.035
10	0	10	9	0	9	8793.590	-0.003
3	3	0	2	2	0	8801.232	-0.006
3	3	1	2	2	1	8807.063	-0.017
9	2	7	8	2	6	8839.176	0.005
6	2	4	5	1	4	8885.759	-0.007
10	2	9	9	2	8	9248.296	0.005
10	7	4	9	7	3	9428.266	0.005
10	7	3	9	7	2	9428.266	0.005
10	6	5	9	6	4	9436.142	0.003
10	6	4	9	6	3	9436.142	0.003
10	5	6	9	5	5	9449.340	0.003
10	5	5	9	5	4	9449.767	0.002
10	3	8	9	3	7	9457.061	-0.002
10	4	7	9	4	6	9469.520	-0.003
10	4	6	9	4	5	9481.890	0.000
10	1	9	9	1	8	9563.222	-0.005
11	1	11	10	1	10	9587.161	-0.007
10	3	7	9	3	6	9616.493	-0.008
11	0	11	10	0	10	9626.048	0.008

4	3	1	3	2	1	9729.665	0.001
4	3	2	3	2	2	9758.256	-0.001
10	2	8	9	2	7	9839.284	-0.010
6	2	5	5	1	5	9961.715	0.000
11	2	10	10	2	9	10138.412	-0.012
11	8	3	10	8	2	10369.286	0.017
11	8	4	10	8	3	10369.286	0.017
11	7	5	10	7	4	10376.002	0.019
11	7	4	10	7	3	10376.002	0.019
11	6	6	10	6	5	10386.479	-0.013
11	6	5	10	6	4	10386.479	-0.013
11	3	9	10	3	8	10397.858	-0.022
11	5	7	10	5	6	10403.896	-0.011
11	5	6	10	5	5	10404.956	-0.014
11	4	8	10	4	7	10427.668	-0.030
11	1	10	10	1	9	10430.152	-0.021
12	1	12	11	1	11	10434.132	-0.009
11	4	7	10	4	6	10451.900	-0.010
12	0	12	11	0	11	10460.416	-0.006
11	3	8	10	3	7	10637.740	-0.016
5	3	3	4	2	3	10721.221	0.006
11	2	9	10	2	8	10824.773	-0.039
12	2	11	11	2	10	11020.652	0.002
12	1	11	11	1	10	11276.875	-0.018
13	1	13	12	1	12	11279.235	-0.017
13	0	13	12	0	12	11296.612	-0.026
12	3	10	11	3	9	11332.980	-0.035
12	5	8	11	5	7	11361.042	-0.026
12	5	7	11	5	6	11363.479	0.009
12	4	9	11	4	8	11387.022	-0.028
12	4	8	11	4	7	11431.130	-0.024
12	2	10	11	2	9	11792.368	-0.048

Table S05. Measured rotational transitions of Rotamer II (TG+T/G+T/c).

J´	$K´_a$	$K´_c$	J´´	$K´´_a$	$K´´_c$	ν_{obs}	ν_{obs}-ν_{cal}
3	2	1	2	1	1	6387.635	0.016
3	2	1	2	1	2	6668.402	0.029
7	1	7	6	0	6	7010.973	0.005
4	2	3	3	1	2	7206.527	-0.008
4	2	2	3	1	2	7288.733	0.014
8	1	8	7	0	7	7799.109	0.002
5	2	4	4	1	3	8006.491	-0.017
3	3	1	2	2	0	8856.184	-0.011
3	3	0	2	2	0	8856.401	0.000
3	3	0	2	2	1	8861.955	-0.011
11	1	10	10	2	9	9573.531	-0.006
4	3	2	3	2	1	9832.342	0.013
4	3	1	3	2	1	9833.777	0.000
4	3	2	3	2	2	9859.997	-0.025
4	3	1	3	2	2	9861.462	-0.008
5	3	2	4	2	3	10874.911	0.018

Table S06. Measured rotational transitions of Rotamer III (TG-T/TT/c).

J´	$K´_a$	$K´_c$	J´´	$K´´_a$	$K´´_c$	ν_{obs}	ν_{obs}-ν_{cal}
4	2	2	3	1	2	6860.239	-0.010
4	2	3	3	1	3	6937.656	0.011
6	1	5	5	0	5	6954.435	-0.011
5	2	3	4	1	3	7803.595	0.004
5	2	4	4	1	4	7931.313	0.029
3	3	0	2	2	0	7950.197	0.008
3	3	1	2	2	1	7950.197	0.008
7	1	6	6	0	6	7970.718	-0.012
4	3	1	3	2	1	8917.100	0.010
4	3	2	3	2	2	8917.734	0.000
6	2	5	5	1	5	8931.539	-0.002
7	2	5	6	1	5	9677.097	-0.016
5	3	2	4	2	2	9883.552	-0.019
5	3	3	4	2	3	9885.500	0.004
6	3	3	5	2	3	10849.256	0.032
6	3	4	5	2	4	10853.711	0.012
4	4	0	3	3	0	10936.780	-0.037
4	4	1	3	3	1	10936.780	-0.037

Figure S04. Comparison of gas phases conformations and crystal phase structure.