

Electronic Supporting Information

**Evidence and Evolution of Criegee Intermediates,
Hydroperoxides and Secondary Organic Aerosols Formed via
Ozonolysis of α -Pinene**

Arnab Bagchi,^{ab} Youqing Yu,^{†a} Jih-Hong Huang,^{ab} and Cheng-Cheng Tsai,^c Wei-Ping Hu,^{*c} and
Chia C. Wang^{*ab}

^aDepartment of Chemistry, National Sun Yat-sen University, Kaohsiung, Taiwan, Republic of China

^bAerosol Science Research Center, National Sun Yat-sen University, Kaohsiung, Taiwan, Republic
of China

^cDepartment of Chemistry and Biochemistry, National Chung Cheng University, Chiayi, Taiwan,
Republic of China

Table of Content:

Supplementary Figures

Figure S1 Optimized structures of α -pinene and its possible ozonolysis intermediates computed at the M06-2X/6-31+G(d,p) level of theory, including: (A) α -pinene, (B) POZ-1, (C) POZ-2, (D) CI-1, (E) CI-2, (F) HP-1, (G) HP-2, (H) SOZ-1 and (I) SOZ-2.

Figure S2 Experimental schematics of the custom-built long-path aerosol cooling chamber integrated to a time-resolved, rapid-scan Fourier transform infrared spectrometer.

Supplementary Tables

Table S1. Computed infrared absorption of α -pinene

Table S2. Computed infrared absorption of POZ, including POZ-1 and POZ-2.

Table S3. Computed infrared absorption of CI, including CI-1 and CI-2.

Table S4. Computed infrared absorption of HP, including HP-1 and HP-2.

Table S5. Computed infrared absorption of SOZ, including SOZ-1 and SOZ-2.

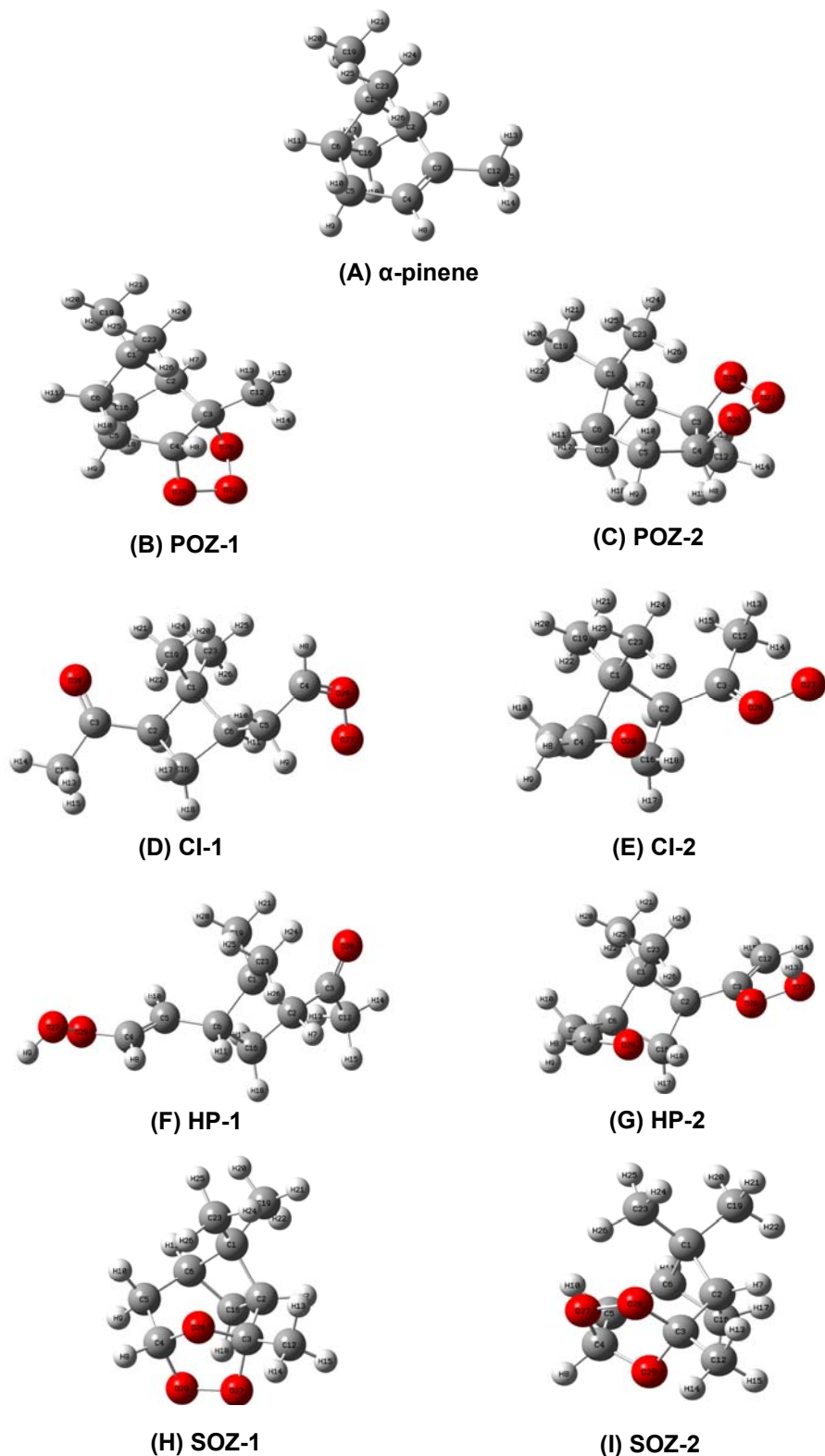


Fig. S1 Optimized structures of α -pinene and its possible ozonolysis intermediates computed at the M06-2X/6-31+G(d,p) level of theory, including: (A) α -pinene, (B) POZ-1, (C) POZ-2, (D) CI-1, (E) CI-2, (F) HP-1, (G) HP-2, (H) SOZ-1 and (I) SOZ-2.

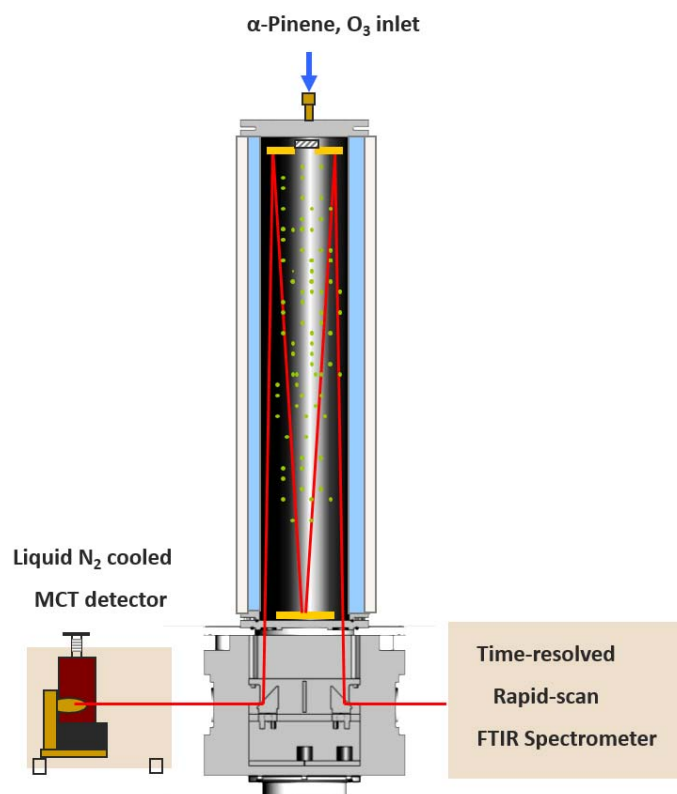


Fig. S2 Experimental schematics of the custom-built long-path aerosol cooling chamber integrated to a time-resolved, rapid-scan Fourier transform infrared spectrometer.

Table S1. Computed infrared absorption of α -pinene.

Calculated IR absorption (cm ⁻¹)	Scaled IR absorption (cm ⁻¹) ^[a]	Calculated Intensity (a.u.)	Vibrational Mode ^[b]	Experimental IR absorption (cm ⁻¹)
806.20	789.27	62.55		
910.78	891.65	16.97	Ring def.	887
974.18	953.73	8.67	Ring def.	954
986.64	965.92	12.06		
1033.77	1012.06	18.08	δ CH ₃	1016
1086.02	1063.22	6.32		
1113.89	1090.50	5.25	δ CH ₂	1090
1135.58	1111.73	8.53		
1157.52	1133.22	9.81	δ CH	1128
1198.02	1172.86	6.38		
1241.09	1215.03	9.47	δ CH ₂	1217
1314.78	1287.17	8.53	δ CH	1270
1368.75	1340.01	6.37	δ CH	1339
1406.92	1377.37	31.65	δ CH ₃	1370
1418.87	1389.07	20.23	δ CH ₃	1379
1421.62	1391.77	26.58	δ CH ₃	1386
1481.64	1450.52	22.66	δ CH ₃	1437
1482.14	1451.01	9.18		
1485.86	1454.66	12.48	δ CH ₃	1447
1497.68	1466.23	22.99	δ CH ₂	1457
1520.95	1489.01	24.57	δ CH ₂	1465
1524.11	1492.11	16.16	δ CH ₂	1473
3038.54	2974.73	56.70	ν CH ₂ s	2846
3043.71	2979.80	39.11		
3048.65	2984.63	22.90		
3052.88	2988.77	74.45	ν CH ₃ s	2893
3071.36	3006.86	33.15		
3084.61	3019.84	48.43		
3088.41	3023.55	86.22	ν CH	2925
3102.43	3037.28	41.71		
3106.45	3041.21	24.40		
3119.18	3053.68	53.54	ν CH ₂ as	2970
3142.21	3076.22	26.33		
3147.99	3081.88	35.29	ν CH	2997
3167.93	3101.40	38.58		
3172.25	3105.63	29.54		
3176.19	3109.49	21.16	ν CH	3034

[a] Scaling factor of 0.979 is used for all scaled IR absorption computations in this work.

Table S2. Computed infrared absorption of POZ, including POZ-1 and POZ-2.

POZ-1		
Calculated IR absorption (cm ⁻¹)	Scaled IR absorption (cm ⁻¹)	Calculated Intensity (a.u.)
840.76	823.10	5.45
864.15	846.00	34.78
889.32	870.64	35.47
903.1	884.13	26.65
920.91	901.57	29.69
941.8	922.02	11.93
947.31	927.42	15.18
963.4	943.17	5.34
980.66	960.07	3.42
985.34	964.65	3.15
1006.52	985.38	2.80
1026.41	1004.86	8.90
1034.22	1012.50	8.79
1047.66	1025.66	33.90
1072.5	1049.98	11.74
1099.9	1076.80	51.62
1122.07	1098.51	23.69
1139.19	1115.27	13.69
1168.51	1143.97	15.80
1180.62	1155.83	58.04
1211.93	1186.48	14.66
1222.08	1196.42	1.27
1261.76	1235.26	9.83
1269.34	1242.68	3.33
1292.47	1265.33	19.32
1300.14	1272.84	4.05
1319.4	1291.69	19.03
1350.83	1322.46	16.31
1361.65	1333.06	4.72
1385.73	1356.63	12.27
1400.05	1370.65	2.28
1410.23	1380.62	32.60
1412.45	1382.79	52.52
1430.56	1400.52	27.98
1486.07	1454.86	14.05
1493.51	1462.15	10.05
1494.50	1463.12	9.61
1500.45	1468.94	29.78
1512.76	1480.99	3.72
1527.93	1495.84	33.39
1530.23	1498.10	17.75
3053.96	2989.83	30.16
3059.42	2995.17	67.85
3068.37	3003.93	9.50
3074.17	3009.61	9.66
3086.1	3021.29	57.89

3088.02	3023.17	23.90
3093.23	3028.27	77.94
3101.69	3036.55	26.65
3120.54	3055.01	9.05
3124.61	3058.99	23.86
3129.48	3063.76	41.20
3147.04	3080.95	27.36
3153.74	3087.51	24.06
3158.08	3091.76	12.12
3173.6	3106.95	31.95

POZ-2

Calculated IR absorption (cm ⁻¹)	Scaled IR absorption (cm ⁻¹)	Calculated Intensity (a.u.)
847	829.21	15.11
877.7	859.27	2.40
894.43	875.65	3.47
899.8	880.90	56.22
911.67	892.52	42.39
937.09	917.41	16.96
952.98	932.97	3.96
963.12	942.89	12.97
971.58	951.18	16.86
985.48	964.78	0.23
1015.67	994.34	2.32
1021.96	1000.50	7.82
1041.59	1019.72	17.57
1059.42	1037.17	5.83
1071.55	1049.05	85.08
1102.88	1079.72	24.53
1105.64	1082.42	13.30
1143.86	1119.84	21.70
1175.54	1150.85	42.16
1180.52	1155.73	35.87
1205.62	1180.30	5.59
1223.33	1197.64	2.58
1254.04	1227.71	3.81
1259.92	1233.46	2.28
1276.65	1249.84	8.78
1291.65	1264.53	23.83
1299.7	1272.41	3.04
1326.34	1298.49	12.68
1345.44	1317.19	10.29
1360.89	1332.31	6.29
1384.37	1355.30	8.39
1395.87	1366.56	2.55
1409.41	1379.81	14.16
1416.65	1386.90	74.64
1426.01	1396.06	27.97

1484.28	1453.11	13.28
1490.72	1459.41	10.53
1495.99	1464.57	35.44
1500.21	1468.71	2.73
1501.58	1470.05	7.89
1514.3	1482.50	2.29
1528.36	1496.26	27.01
1533.67	1501.46	22.25
3054.24	2990.10	25.19
3058.12	2993.90	46.98
3070.46	3005.98	14.85
3074.22	3009.66	21.30
3081.83	3017.11	28.23
3091.18	3026.27	79.53
3093.1	3028.14	31.92
3121.99	3056.43	15.99
3123.31	3057.72	9.76
3128.43	3062.73	50.43
3128.77	3063.07	19.19
3150.2	3084.05	29.75
3151.03	3084.86	30.09
3152.53	3086.33	24.57
3176.68	3109.97	8.96
3180.89	3114.09	18.92

Table S3. Computed infrared absorption of CI, including CI-1 and CI-2.

CI-1		
Calculated IR absorption (cm ⁻¹)	Scaled IR absorption (cm ⁻¹)	Calculated Intensity (a.u.)
762.24	746.23	0.97
864.04	845.90	40.09
897.22	878.37	58.45
918.88	899.58	2.36
941.15	921.39	34.05
960.40	940.23	8.93
965.43	945.16	374.70
976.77	956.25	7.10
991.57	970.75	28.09
1016.55	995.20	10.17
1024.41	1002.89	92.38
1038.70	1016.89	58.27
1060.67	1038.40	65.27
1099.50	1076.41	0.66
1117.57	1094.10	1.66
1149.66	1125.52	9.76
1177.73	1153.00	2.28
1197.35	1172.20	26.40
1209.88	1184.47	13.14
1241.66	1215.59	205.75
1251.55	1225.27	43.44
1267.47	1240.85	23.72
1279.77	1252.89	9.13
1296.10	1268.89	12.59
1326.98	1299.11	11.36
1355.03	1326.57	20.36
1380.59	1351.60	53.59
1396.52	1367.19	110.05
1402.50	1373.05	115.57
1416.55	1386.80	100.51
1425.99	1396.05	23.32
1468.55	1437.71	28.72
1470.69	1439.81	36.08
1482.82	1451.69	41.09
1488.33	1457.08	2.01
1499.90	1468.41	5.96
1501.76	1470.22	30.03
1514.89	1483.08	27.32
1520.18	1488.25	31.86
1666.37	1631.38	5.34
1846.11	1807.35	350.75
3045.69	2981.73	24.18
3055.41	2991.25	30.16
3058.55	2994.32	7.09
3060.63	2996.36	10.28
3063.69	2999.35	1.78
3066.31	3001.92	9.83

3081.55	3016.84	35.93
3122.53	3056.96	26.57
3134.51	3068.69	26.08
3136.38	3070.52	5.12
3136.70	3070.83	13.22
3144.22	3078.19	2.69
3147.28	3081.19	34.34
3161.26	3094.87	7.97
3187.13	3120.20	7.80
3195.33	3128.23	3.39

CI-2

Calculated IR absorption (cm ⁻¹)	Scaled IR absorption (cm ⁻¹)	Calculated Intensity (a.u.)
782.39	765.96	43.22
894.19	875.41	73.37
904.62	885.62	54.49
940.66	920.91	23.50
944.65	924.81	102.17
961.57	941.38	0.31
985.30	964.61	73.65
995.37	974.46	25.96
1000.49	979.48	55.37
1018.32	996.93	3.83
1041.00	1019.14	35.10
1055.66	1033.49	84.79
1088.29	1065.44	20.16
1132.96	1109.16	27.12
1160.80	1136.43	13.16
1177.77	1153.03	31.67
1195.26	1170.16	14.86
1232.60	1206.72	15.49
1243.12	1217.02	38.92
1257.73	1231.32	64.82
1276.11	1249.31	37.23
1301.23	1273.90	8.31
1334.80	1306.77	22.68
1378.39	1349.45	63.23
1388.51	1359.35	66.62
1406.21	1376.68	32.54
1410.97	1381.34	47.19
1420.24	1390.41	51.64
1428.33	1398.34	43.17
1438.20	1407.99	39.85
1442.59	1412.30	14.13
1451.01	1420.54	22.10
1487.95	1456.71	0.31
1492.13	1460.80	9.67
1493.17	1461.81	79.71
1506.88	1475.24	17.93

1513.25	1481.48	32.67
1519.36	1487.45	55.76
1643.76	1609.24	26.45
1877.95	1838.51	277.24
2975.96	2913.46	175.42
3032.50	2968.81	47.19
3048.01	2984.00	21.07
3054.13	2990.00	36.61
3057.75	2993.54	34.55
3060.79	2996.52	7.30
3065.18	3000.81	10.47
3066.60	3002.20	24.08
3114.69	3049.28	29.23
3119.29	3053.78	18.65
3121.98	3056.42	0.11
3123.91	3058.31	43.79
3132.41	3066.63	32.10
3168.38	3101.84	5.20
3185.55	3118.65	6.04
3190.70	3123.70	6.33

Table S4. Computed infrared absorption of HP, including HP-1 and HP-2.

HP-1		
Calculated IR absorption (cm ⁻¹)	Scaled IR absorption (cm ⁻¹)	Calculated Intensity (a.u.)
805.33	788.41	24.57
870.47	852.19	27.41
898.09	879.23	30.65
920.61	901.28	3.06
952.22	932.22	0.31
964.46	944.21	51.84
968.40	948.06	173.23
979.99	959.41	20.55
1005.62	984.50	80.25
1006.47	985.34	1.94
1027.65	1006.07	10.33
1035.49	1013.74	6.81
1097.16	1074.12	3.86
1110.60	1087.28	13.29
1156.17	1131.89	69.68
1180.74	1155.94	3.96
1183.18	1158.33	210.19
1198.16	1173.00	24.24
1225.74	1200.00	33.54
1243.33	1217.22	172.60
1246.02	1219.86	55.27
1274.14	1247.38	21.14
1288.15	1261.10	9.98
1310.70	1283.18	8.39

1327.56	1299.68	8.66
1358.45	1329.93	20.24
1395.04	1365.74	167.71
1401.62	1372.18	35.74
1416.65	1386.90	125.89
1421.08	1391.24	278.03
1425.26	1395.33	57.93
1466.60	1435.80	34.59
1475.88	1444.89	38.31
1488.47	1457.21	0.53
1498.15	1466.69	1.38
1502.36	1470.81	25.31
1511.81	1480.06	34.13
1518.83	1486.93	27.60
1764.00	1726.95	190.13
1841.21	1802.54	376.63
3048.45	2984.44	33.70
3052.55	2988.45	30.22
3055.58	2991.41	2.55
3061.53	2997.24	1.89
3070.10	3005.62	13.97
3080.34	3015.66	37.26
3122.86	3057.28	16.11
3124.47	3058.86	55.42
3134.10	3068.29	3.45
3141.50	3075.52	11.41
3142.30	3076.32	43.39
3162.23	3095.82	13.15
3182.12	3115.30	10.66
3182.74	3115.90	8.77
3222.96	3155.28	10.28
3849.85	3769.00	112.42

HP-2

Calculated IR absorption (cm ⁻¹)	Scaled IR absorption (cm ⁻¹)	Calculated Intensity (a.u.)
805.33	788.41	24.57
866.76	848.56	302.60
870.47	852.19	27.41
898.09	879.23	30.65
900.05	881.15	71.89
919.80	900.48	16.49
920.61	901.28	3.06
941.98	922.20	21.62
945.07	925.23	78.17
965.62	945.34	0.71
990.25	969.45	43.32
1000.00	979.00	3.97
1010.13	988.92	7.06
1038.57	1016.76	9.72

1066.55	1044.15	10.51
1087.00	1064.17	17.32
1138.28	1114.37	0.07
1161.45	1137.06	12.49
1189.85	1164.87	17.25
1198.60	1173.43	17.27
1240.11	1214.07	17.91
1249.41	1223.17	18.11
1265.26	1238.69	26.40
1304.90	1277.49	0.36
1325.38	1297.54	52.30
1331.26	1303.31	50.86
1349.79	1321.45	66.84
1379.93	1350.95	55.84
1406.04	1376.51	3.79
1408.88	1379.29	13.94
1416.90	1387.15	164.53
1424.71	1394.79	50.77
1434.13	1404.01	21.10
1444.37	1414.04	98.17
1449.09	1418.66	16.69
1489.81	1458.53	6.77
1495.66	1464.25	4.40
1508.29	1476.62	9.85
1517.65	1485.78	25.84
1522.96	1490.98	61.63
1748.07	1711.36	255.41
1871.31	1832.02	299.46
2961.99	2899.79	195.31
3029.15	2965.54	49.06
3040.57	2976.71	25.08
3048.87	2984.84	48.90
3053.83	2989.70	38.44
3061.56	2997.27	12.57
3093.83	3028.86	15.39
3104.85	3039.65	46.32
3111.32	3045.98	12.41
3116.58	3051.13	59.91
3124.62	3059.00	37.06
3189.55	3122.57	5.63
3194.25	3127.17	5.18
3210.16	3142.75	3.02
3311.49	3241.95	0.95
3831.61	3751.14	65.86

Table S5. Computed infrared absorption of SOZ, including SOZ-1 and SOZ-2.

SOZ-1		
Calculated IR absorption (cm ⁻¹)	Scaled IR absorption (cm ⁻¹)	Calculated Intensity (a.u.)
801.03	784.21	71.61
812.36	795.30	0.63
852.62	834.71	20.07
858.70	840.66	68.63
886.77	868.14	27.62
903.52	884.55	60.16
909.15	890.06	8.55
933.45	913.85	27.31
942.04	922.26	34.29
957.64	937.53	26.25
970.43	950.05	13.46
986.88	966.16	14.49
1004.78	983.68	8.17
1030.06	1008.43	49.46
1041.45	1019.58	11.87
1068.91	1046.46	77.71
1096.59	1073.56	31.23
1123.47	1099.88	21.54
1140.85	1116.89	58.88
1159.09	1134.75	99.19
1192.75	1167.70	74.01
1206.85	1181.51	148.00
1221.77	1196.11	105.03
1228.20	1202.41	86.67
1237.84	1211.84	43.62
1256.34	1229.96	22.24
1270.09	1243.42	62.77
1289.08	1262.01	37.52
1313.53	1285.94	22.87
1324.54	1296.72	53.64
1361.49	1332.90	47.51
1377.34	1348.41	9.51
1394.46	1365.18	22.92
1406.73	1377.18	16.56
1415.41	1385.69	43.30
1421.86	1392.00	42.79
1426.44	1396.49	83.09
1472.95	1442.02	23.95
1485.88	1454.68	4.55
1490.59	1459.28	6.00
1494.81	1463.42	13.28
1496.04	1464.63	5.37
1507.01	1475.36	5.38
1524.21	1492.20	27.18
1533.51	1501.31	30.73
3053.71	2989.58	19.69
3058.72	2994.49	54.96

3059.57	2995.32	23.31
3072.74	3008.21	79.19
3081.03	3016.33	14.72
3085.84	3021.03	26.93
3107.21	3041.96	17.44
3115.31	3049.89	17.71
3125.80	3060.16	45.69
3130.48	3064.74	68.29
3132.83	3067.04	14.57
3154.89	3088.64	51.19
3171.09	3104.50	8.96
3186.94	3120.01	9.05
3206.29	3138.96	4.75
3212.91	3145.44	10.80

SOZ-2

Calculated IR absorption (cm ⁻¹)	Scaled IR absorption (cm ⁻¹)	Calculated Intensity (a.u.)
821.46	804.21	1.49
851.39	833.51	12.81
867.74	849.52	14.14
885.75	867.15	8.43
893.94	875.16	66.08
900.78	881.86	69.23
925.24	905.81	49.99
955.78	935.70	36.67
969.40	949.05	13.77
978.51	957.96	14.80
987.61	966.87	22.58
1009.13	987.94	10.24
1028.02	1006.43	25.41
1034.61	1012.89	21.27
1072.39	1049.87	84.42
1097.42	1074.37	16.05
1120.23	1096.70	36.50
1150.32	1126.17	32.58
1168.73	1144.19	113.57
1184.02	1159.16	114.52
1198.62	1173.44	105.61
1209.69	1184.28	132.32
1226.81	1201.04	78.37
1236.25	1210.29	29.94
1261.13	1234.65	13.41
1267.17	1240.56	68.13
1284.25	1257.28	76.77
1317.13	1289.47	1.42
1324.27	1296.46	47.08
1361.95	1333.35	57.15
1378.75	1349.79	0.72
1398.68	1369.31	16.02

1407.66	1378.10	17.09
1412.42	1382.76	52.59
1420.94	1391.10	83.11
1429.84	1399.82	29.97
1471.92	1441.01	24.53
1485.55	1454.35	2.38
1490.59	1459.28	8.09
1492.49	1461.15	13.35
1497.57	1466.12	4.77
1504.57	1472.98	18.77
1520.51	1488.58	17.22
1531.31	1499.15	29.78
3053.01	2988.90	15.51
3057.02	2992.82	4.67
3058.05	2993.83	89.84
3069.92	3005.46	83.47
3075.91	3011.31	4.07
3084.20	3019.44	37.62
3105.65	3040.43	15.65
3119.63	3054.12	4.95
3123.50	3057.91	20.67
3127.15	3061.48	51.66
3140.21	3074.27	42.25
3149.84	3083.69	48.53
3162.61	3096.20	8.47
3180.62	3113.83	0.46
3181.36	3114.55	29.51
3228.17	3160.38	3.13
