Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Transient UV Pump-IR Probe Investigation of Heterocyclic Ring-Opening Dynamics in the Solution Phase: The Role Played by nσ* States in the Photoinduced Reactions of Thiophenone and Furanone

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Electronic Supplementary Information

Table S1. Harmonic and anharmonic vibrational wavenumbers calculated for thiophenone and three possible ring-opened structures at the MP2/6-311+G(*d,p*) level of theory

Parent			**Aldehyde**			**Enol**			**Epoxy**		
Harmonic wavenumber (cm^{-1})	*Intensity* ($km\ mol^{-1}$)	*Anharmonic wavenumber* (cm^{-1})	*Harmonic wavenumber* (cm^{-1})	*Intensity* ($km\ mol^{-1}$)	*Anharmonic wavenumber* (cm^{-1})	*Harmonic wavenumber* (cm^{-1})	*Intensity* ($km\ mol^{-1}$)	*Anharmonic wavenumber* (cm^{-1})	*Harmonic wavenumber* (cm^{-1})	*Intensity* ($km\ mol^{-1}$)	*Anharmonic wavenumber* (cm^{-1})
3257.0	1	3102.6	3217.8	8	3080.5	3232.4	4	3087.1	3260.8	2	3113.3
3222.4	2	3094.7	3116.7	25	2986.1	3224.4	13	3093.1	3236.9	13	3103.1
3145.9	1	2997.6	3070.1	5	2911.8	3198.3	7	3074.1	3192.5	2	3057.5
3093.0	7	2994.4	3025.2	19	2926.0	2779.4	1	2676.8	3161.5	9	3077.2
1749.7	379	1720.5	2197.8	474	2154.2	2197.0	628	2155.4	2205.9	778	2159.5
1648.9	1	1593.6	1469.5	4	1440.7	1643.6	46	1584.2	1515.2	11	1497.4
1474.6	8	1451.0	1433.3	8	1401.9	1438.6	34	1406.8	1460.7	34	1420.8
1361.8	11	1332.6	1400.5	11	1372.2	1377.3	11	1344.1	1300.2	4	1272.2
1298.1	4	1261.4	1362.0	20	1329.7	1227.8	0	1206.4	1217.0	6	1191.0
1147.5	35	1118.7	1210.2	3	1177.7	1144.7	0	1124.0	1174.6	4	1140.7
1143.2	6	1121.2	1190.4	19	1171.0	976.0	14	954.0	1123.2	13	1097.4
1088.3	55	1066.4	1138.3	5	1117.2	940.2	12	920.4	1116.2	9	1088.9
982.1	5	963.1	974.9	14	932.4	913.9	12	902.3	1051.6	26	1046.9
948.6	0	943.6	952.4	10	938.2	833.4	10	808.3	967.3	3	948.2
928.7	3	910.8	840.7	17	821.2	717.0	7	705.4	912.3	2	890.5
801.6	10	787.4	738.1	1	713.8	688.6	27	683.7	714.9	2	701.9
761.5	40	761.8	709.7	2	703.8	533.1	22	533.9	658.3	76	644.4
692.4	1	681.9	527.4	8	511.0	512.9	3	504.3	593.4	8	581.7
641.7	53	630.2	497.7	13	488.6	482.1	60	509.9	520.3	4	514.7
581.8	7	579.1	432.7	60	437.7	406.3	5	403.5	513.4	29	509.8
519.9	2	512.6	243.3	12	243.0	234.3	36	224.2	370.4	1	367.6
413.3	4	408.2	159.5	1	140.1	203.3	14	190.7	273.8	11	270.6
301.0	2	308.7	136.5	1	138.7	135.8	0	133.3	154.3	1	152.8
138.4	0	139.9	32.3	2	14.0	72.7	0	63.9	50.5	1	44.4

Table S2. Harmonic and anharmonic vibrational wavenumbers calculated for furanone and three possible ring-opened structures at the MP2/6-311+G(*d,p*) level of theory

Parent			**Aldehyde**			**Enol**			**Epoxy**		
Harmonic wavenumber (cm^{-1})	*Intensity* ($km\ mol^{-1}$)	*Anharmonic wavenumber* (cm^{-1})	*Harmonic wavenumber* (cm^{-1})	*Intensity* ($km\ mol^{-1}$)	*Anharmonic wavenumber* (cm^{-1})	*Harmonic wavenumber* (cm^{-1})	*Intensity* ($km\ mol^{-1}$)	*Anharmonic wavenumber* (cm^{-1})	*Harmonic wavenumber* (cm^{-1})	*Intensity* ($km\ mol^{-1}$)	*Anharmonic wavenumber* (cm^{-1})
3379.5	0	3254.8	3233.7	9	3104.3	3905.7	109	3723.3	3245.4	11	3110.6
3286.8	1	3145.9	3080.0	5	2930.0	3256.4	7	3122.1	3244.0	21	3098.5
3145.0	9	2996.7	3047.2	44	2962.8	3236.7	15	3104.3	3176.5	12	3047.7
3093.2	19	2947.0	2983.7	94	2848.7	3225.0	1	3069.5	3142.5	21	3037.5
1838.0	418	1805.5	2211.4	531	2167.9	2200.7	641	2159.8	2209.2	693	2169.7
1639.2	1	1599.3	1765.1	73	1742.3	1713.2	27	1675.4	1553.7	13	1559.0
1514.1	6	1501.5	1473.6	13	1463.2	1447.4	32	1414.5	1486.8	50	1446.0
1387.9	15	1352.4	1440.5	6	1406.6	1399.7	1	1368.0	1323.8	0	1298.9
1349.9	11	1319.0	1403.9	8	1373.2	1279.2	97	1246.5	1303.5	9	1273.4
1221.4	0	1194.4	1373.6	26	1327.9	1227.9	18	1211.2	1190.9	7	1164.8
1160.4	125	1127.9	1222.6	0	1200.4	1144.9	16	1118.3	1174.0	1	1142.5
1123.3	75	1095.6	1144.4	6	1133.2	1062.9	45	1043.2	1164.9	9	1142.9
1056.9	32	1037.4	1053.6	1	1029.0	939.5	9	918.7	1105.7	6	1095.4
1028.2	10	1008.1	982.9	3	964.3	842.9	3	875.3	1091.3	8	1075.6
963.6	1	948.4	881.9	42	859.7	820.6	18	814.0	961.5	36	938.0
909.1	0	918.8	817.5	1	795.1	703.8	64	704.7	864.2	31	842.3
879.5	48	859.8	726.2	1	713.7	579.1	1	565.1	806.7	46	779.9
790.6	3	777.6	569.1	0	562.1	510.4	8	538.3	611.6	5	601.4
778.0	42	788.9	530.5	6	532.7	506.4	14	535.7	552.9	35	548.8
691.4	1	681.4	439.8	66	448.6	433.6	41	470.2	531.4	8	525.4
632.2	13	628.8	280.5	22	276.3	273.8	146	189.8	377.2	4	376.5
492.8	2	486.6	169.8	4	173.3	254.7	21	232.6	345.7	25	346.5
316.8	6	330.5	162.9	4	160.5	143.9	2	137.7	157.8	1	156.1
185.8	1	187.5	63.3	3	81.1	82.1	0	88.8	57.0	2	56.6

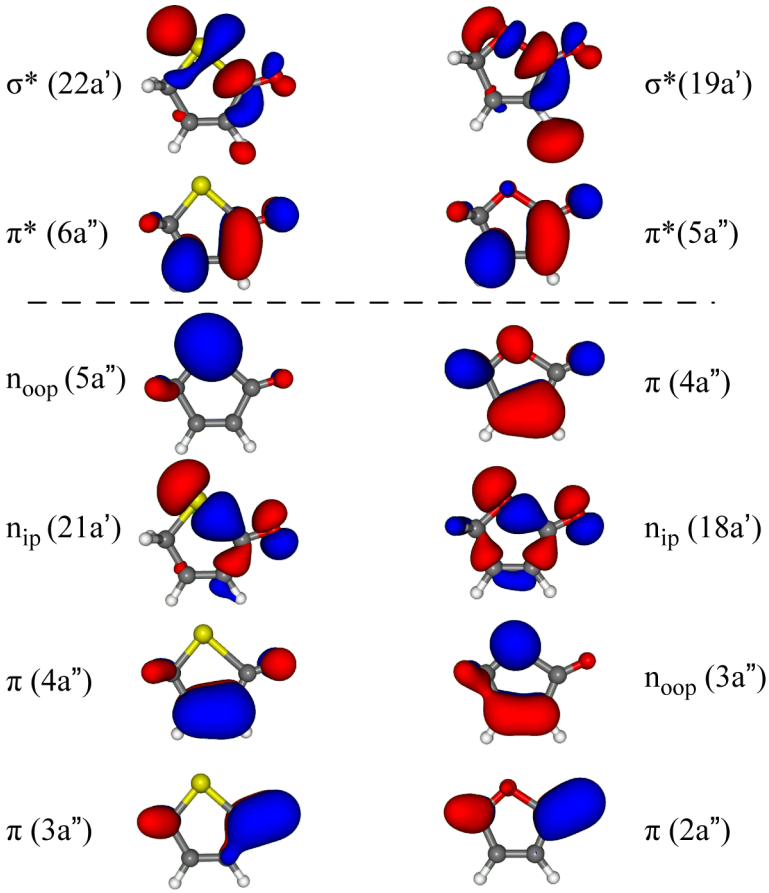

Figure S1. Orbitals comprising the active spaces used in the CASSCF calculations of thiophenone (left) and furanone (right). The orbitals are presented in energetic order, increasing from bottom to top. n_{ip} = in-plane non-bonding orbital, n_{oop} = out-of-plane non-bonding orbital. Isolines are drawn at a value of 0.05.

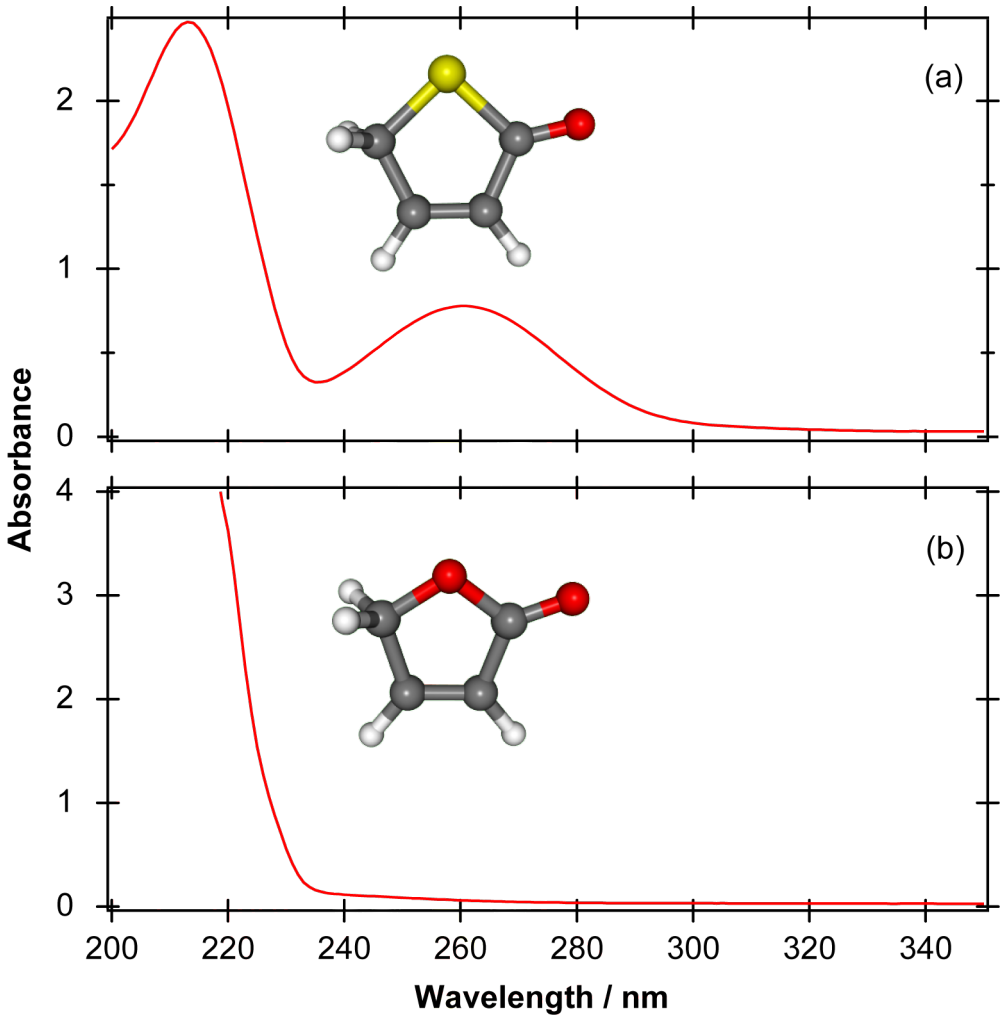

Figure S2. UV-visible absorption spectra of (a) 23 mM thiophenone dissolved in CD_3CN, and (b) 50 mM furanone in dichloromethane. The pathlength was 100 μm for both spectra.

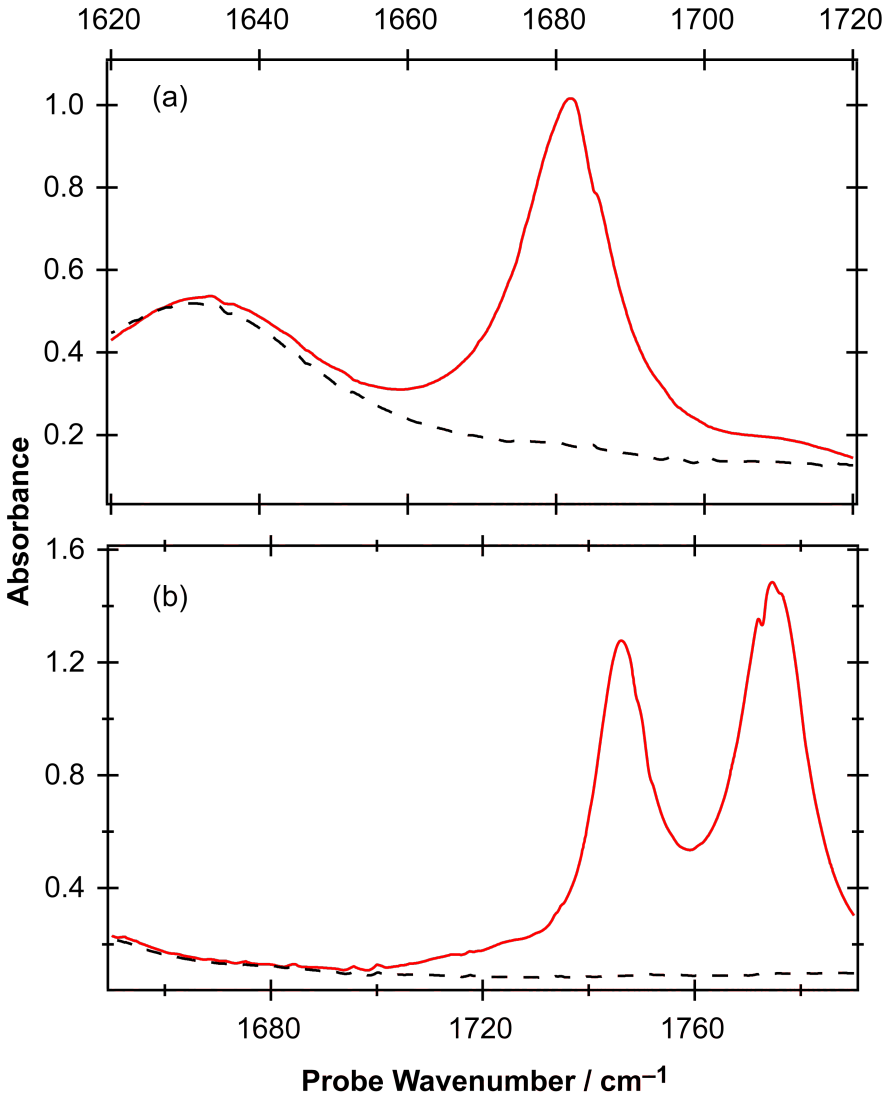

Figure S3. FTIR absorption spectra of (a) 100 mM thiophenone dissolved in CH_3CN, and (b) 250 mM furanone in CH_3CN. Both spectra were recorded using a 100 μm pathlength Harrick cell. The abscissae have been scaled so as to cover the same range as figures 1(a) and 2(a). The dashed black line in (a) and (b) is the signal from the CH_3CN solvent