SUPPLEMENTARY MATERIAL (SM) FOR:

The ionic and ground states of gamma-pyrone. The photoionization spectrum studied by synchrotron radiation, and interpreted by configuration interaction and density functional calculations.

Michael H. Palmer,[1,a] Marcello Coreno,[2,b] Monica de Simone,[3,b] Cesare Grazioli.[3,b] Nykola C. Jones,[4,b] Søren Vrønning Hoffmann,[4,b] R. Alan Aitken[5,b] and Dheirya K. Sonecha.[5,b]

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Table SM1. Peak positions from the multi-peak analysis for the combined lowest band, assigned to the combined $^2B_2$ + $^2B_1$ ionization, and the next band assigned to the $^2A_2$ state. Gaussian peaks, with numbers shown in Figure 3, are labelled Gn where n = 0 to 13. The overlapping nature of the onset to the PES is discussed below. Total peak area = 506 ± 8.8. Total fitted points: 798

PES Band 9.0 to 10.4 eV				
Type	Location	LocSigma	DeltaG0	DeltaG5
G0	9.230	0.002		
G1s	9.292	0.001	0.062	
G2	9.352	0.001	0.06	
G3	9.409	0.001	0.057	
G4	9.457	0.001	0.048	
G5	9.491	0.001		0
G6	9.513	0.001	0.056	
G7	9.552	0.001		0.061
G8	9.573	0.001		
G9	9.613	0.001		0.061
G10	9.633	0.001	0.06	
G11	9.652	0.002		
G12	9.688	0.001		0.075
G13	9.748	0.001		
Lorentzian_bckg	9.664	0.004		0.06
PES Band 10.8 to 11.3 eV				
Type	Location	LocSigma		
L0	10.826	0.001		
L1	10.841	0.001		
L2	10.897	0.001		
L3	10.953	0.002		
L4	10.988	0.001		
L5	11.028	0.001		
L6	11.086	0.001		
L7	11.215	0.001		

Figure SM2. The calculated structures for the ionic states.

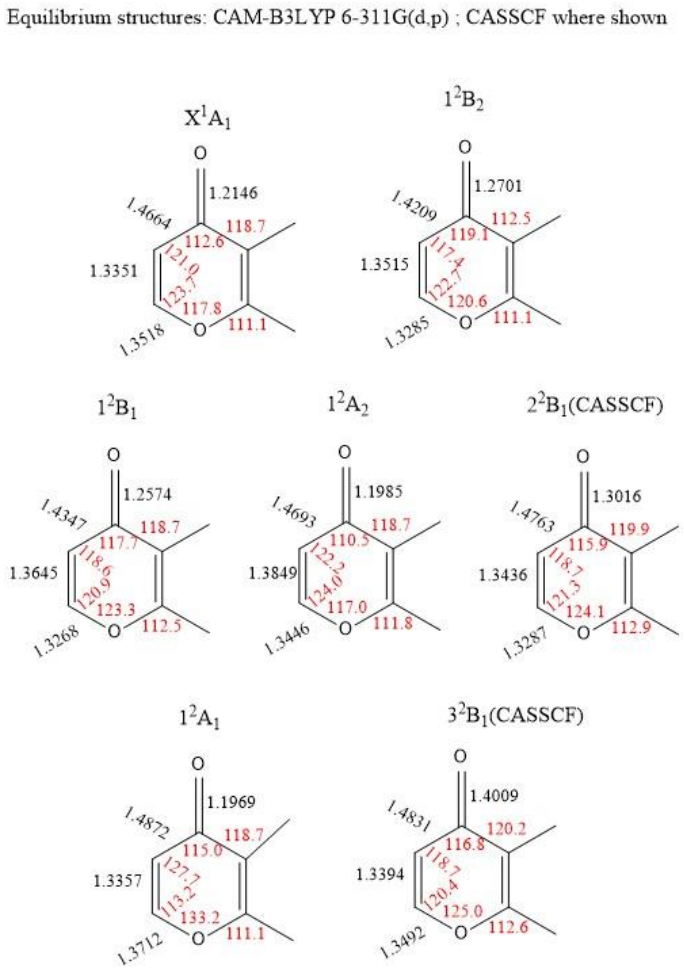

Table SM3. The integrated electron density in the atomic basins, defined by the critical points as indicated in Figure 4, for both the ground and lowest ionic state. Electron density differences between the ground and ionic states at individual atomic centres were obtained by the atoms in molecules (AIM) procedure.

Integrated electron density in the nuclear basin using the CAM-B3LYP method with the 6-311G(d,p) basis set.					Nuclear basin electron density difference from that in the X^1A_1 state		
Atom	X^1A_1	1^2B_2	1^2B_1	1^2A_2	1^2B_2	1^2B_1	1^2A_2
O_4	-1.111	-0.554	-0.750	-1.016	0.557	0.361	0.095
C_4	1.015	0.654	0.863	1.119	-0.361	-0.152	0.105
H_3	0.070	0.159	0.175	0.181	0.089	0.105	0.111
C_3	-0.019	0.062	0.042	0.017	0.081	0.061	0.036
H_2	0.083	0.182	0.189	0.205	0.098	0.106	0.122
C_2	0.464	0.581	0.551	0.579	0.116	0.087	0.114
O_1	-1.101	-1.065	-1.026	-1.068	0.035	0.075	0.033

Table SM4. The higher energy region of the photoelectron spectrum of γ-pyrone determined with the scaled symmetry-adapted cluster CI (SAC-CI) theoretical pole strength intensities.

SAC-CI calc. IE / eV	SAC-CI scaled IE / eV	Intensity	Symmetry
18.180	17.602	0.004	A2
18.343	17.752	0.002	B2
18.403	17.807	0.039	B1
18.433	17.835	0.009	A1
19.346	18.676	0.003	A2
19.648	18.954	0.006	A1
20.114	19.383	0.008	B2
20.142	19.409	0.009	B1
20.625	19.854	0.041	B2
20.781	19.997	0.001	B1
21.078	20.271	0.038	B1
21.162	20.348	0.003	A2
21.760	20.899	0.014	B2
21.907	21.034	0.003	A2
22.171	21.277	0.002	A1
22.411	21.498	0.000	A2
22.766	21.825	0.000	A2
22.834	21.888	0.016	B1
22.910	21.958	0.000	B1
22.913	21.961	0.000	A1
23.403	22.412	0.016	B1
23.786	22.765	0.002	A2
24.169	23.117	0.000	A2
24.443	23.370	0.000	A2

Table SM5. The ascending sequence of harmonic frequencies for the 1^2B_2 state with the normal modes labels.

	1	2	3
	18B1	27B2	13A2
Frequencies --	197.9629	385.5111	395.1142
	4	5	6
	10A1	17B1	26B2
Frequencies --	500.7414	508.9324	671.9674
	7	8	9
	16B1	15B1	9A1
Frequencies --	721.7018	853.8121	858.8998
	10	11	12
	12A2	8A1	14B1
Frequencies --	861.2602	961.4754	997.8925
	13	14	15
	11A2	7A1	25B2
Frequencies --	1000.7354	1059.7949	1095.2109
	16	17	18
	6A1	24B2	23B2
Frequencies --	1243.7553	1251.5543	1366.1904
	19	20	21
	5A1	4A1	22B2
Frequencies --	1391.5683	1446.0348	1474.6392
	22	23	24
	21B2	3A1	20B2
Frequencies --	1555.3079	1684.1216	3241.2320
	25	26	27
	2A1	19B2	1A1
Frequencies --	3242.1730	3253.3529	3256.2498

Table SM6. The ascending sequence harmonic frequencies for the 1^2B_1 state with the normal modes labels.

	1	2	3
	18B1	13A2	27B2
Frequencies --	185.3777	375.9044	438.7943
	4	5	6
	17B1	10A1	26B2
Frequencies --	495.2988	510.1166	662.4249
	7	8	9
	16B1	9 A1	15B1
Frequencies --	732.5419	826.3411	864.5875
	10	11	12
	12A2	8A1	14B1
Frequencies --	871.2053	963.5861	1006.2271
	13	14	15
	25B2	11A2	7A1
Frequencies --	1016.8518	1033.8945	1038.8893
	16	17	18
	24B2	6A1	5A1
Frequencies --	1105.4299	1202.1297	1283.8432
	19	20	21
	23B2	22B2	4A1
Frequencies --	1304.0469	1442.7747	1450.5341
	22	23	24
	21B2	3A1	20B2
Frequencies --	1522.7208	1636.6081	3233.0720
	25	26	27
	2A1	19B2	1A1
Frequencies --	3233.5326	3251.5418	3255.0764

Table SM7. The ascending sequence harmonic frequencies for the 1^2A_2 state with the normal modes labels.

	1	2	3
	18B1	13A2	17B1
Frequencies --	-55.9378	289.4276	320.3156
	4	5	6
	27B2	10A1	26B2
Frequencies --	445.7243	495.8675	622.9599
	7	8	9
	16B1	9A1	12A2
Frequencies --	647.1962	809.8822	814.9418
	10	11	12
	15B1	8A1	11A2
Frequencies --	871.7393	957.8255	989.8998
	13	14	15
	14B1	25B2	7A1
Frequencies --	996.4415	1015.8775	1023.6122
	16	17	18
	6A1	24B2	23B2
Frequencies --	1227.9524	1233.8029	1378.7412
	19	20	21
	22B2	5A1	4A1
Frequencies --	1435.1450	1438.5629	1614.2254
	22	23	24
	3A1	21B2	20B2
Frequencies --	1828.9324	2093.8376	3212.7654
	25	26	27
	2A1	19B2	1A1
Frequencies --	3213.0478	3228.1642	3230.9083

Table SM8. The ascending sequence harmonic frequencies for the 2^2B_1 state with the normal modes labels.

	1	2	3
	18B1	13A2	27B2
Frequencies --	153.0724	418.9781	446.6424
	4	5	6
	17B1	10A1	26B2
Frequencies --	500.3338	509.7334	704.7423
	7	8	9
	16B1	9A1	12A2
Frequencies --	707.3472	829.6858	1017.1800
	10	11	12
	8A1	14B1	7A1
Frequencies --	1020.1691	1052.6049	1071.8316
	13	14	15
	25B2	14B1	11A2
Frequencies --	1158.4891	1177.1867	1184.9352
	16	17	18
	6A1	24B2	23B2
Frequencies --	1293.7527	1332.5728	1495.5795
	19	20	21
	5A1	22B2	4A1
Frequencies --	1516.7398	1560.9009	1711.6107
	22	23	24
	3A1	21B2	20B2
Frequencies --	1966.6986	2038.2310	3378.8580
	25	26	27
	2A1	19B2	1A1
Frequencies --	3379.3158	3418.5615	3421.7648

Table SM9. The ascending sequence harmonic frequencies for the 1^2A_1 state with the normal modes labels.

	1	2	3
	18B1	17B1	27B2
Frequencies --	46.4796	228.4407	387.1319
	4	5	6
	13A2	10A1	26B2
Frequencies --	415.9264	477.5105	541.9100
	7	8	9
	16B1	9A1	8A1
Frequencies --	706.8287	719.4481	767.6080
	10	11	12
	15B1	25B2	12A2
Frequencies --	837.2969	902.1302	908.2856
	13	14	15
	7A1	14 B1	11A2
Frequencies --	926.1650	945.4204	1020.0373
	16	17	18
	24B2	6A1	23B2
Frequencies --	1103.0507	1145.4758	1216.0536
	19	20	21
	5A1	22 B2	21B2
Frequencies --	1288.8184	1307.4905	1567.4992
	22	23	24
	4A1	3A1	20B2
Frequencies --	1602.5136	1820.3101	3117.0536
	25	26	27
	2A1	19B2	1A1
Frequencies --	3144.9922	3190.4817	3202.2266

Table SM10. The ascending sequence harmonic frequencies for the 3^2B_1 state with the normal modes labels.

	1	2	3
	18B1	17B1	27B2
Frequencies --	-280.8971	150.3781	386.9291
	4	5	6
	13A2	10A1	16B1
Frequencies --	434.9866	475.9309	563.0435
	7	8	9
	26B2	9A1	15B1
Frequencies --	698.9052	770.5598	803.8035
	10	11	12
	12A2	8A1	11A2
Frequencies --	827.7082	953.1238	1017.0949
	13	14	15
	7A1	14B1	25B2
Frequencies --	1034.6282	1035.3238	1155.5926
	16	17	18
	6A1	24B2	5A1
Frequencies --	1258.8028	1298.0024	1387.2993
	19	20	21
	23B2	22B2	4A1
Frequencies --	1482.0010	1515.2040	1533.0979
	22	23	24
	3A1	21B2	20B2
Frequencies --	1799.2183	2166.3049	3374.8524
	25	26	27
	2A1	19B2	1A1
Frequencies --	3375.9289	3427.6924	3433.7167

SM11. The transition state between the 1^2B_2 and 1^2B^1 ionic states including the labelled strucutre.

Optimized Parameters (Angstrom and degrees)

Definition	TS	Reactant 1	Reactant 2
R14	1.3226	1.3285	1.3268
R15	1.3226	1.3285	1.3268
R23	1.1685	1.2701	1.2574
R28	1.4803	1.4209	1.4347
R29	1.4803	1.4209	1.4347
R46	1.0810	1.0818	1.0817
R48	1.4126	1.3515	1.3645
R57	1.0810	1.0818	1.0817
R59	1.4126	1.3515	1.3645
R810	1.0864	1.0805	1.0826
R911	1.0864	1.0805	1.0826
A415	112.8142	120.5597	123.3026
A328	142.2222	120.4431	121.1589
A329	142.2222	120.4431	121.1589
A829	73.9541	119.1138	117.6821
A146	116.1886	112.5364	112.5257

A148	114.7610	122.7398	120.8703
A648	128.9275	124.7238	126.6040
A157	116.1886	112.5364	112.5257
A159	114.7610	122.7398	120.8703
A759	128.9275	124.7238	126.6040
A284	116.4087	117.4235	118.6374
A2810	118.0520	121.2254	120.0378
A4810	122.4092	121.3511	121.3248
A295	116.4087	117.4235	118.6374
A2911	118.0520	121.2254	120.0378
A5911	122.4092	121.3511	121.3248

The atomic labelling used in SM11: