

## Supplementary Information

### Oxidative damage in DNA base revealed by UV Resonant Raman spectroscopy

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In the following tables are reported the comparisons between experimental (pristine and oxidized nucleotides aqueous solutions, as reported in the main work) and the simulated (nitrogenous bases with a terminal CH<sub>3</sub>) frequency band positions. The letters within the brackets near the peak experimental position indicates the peaks intensities, empirically designates as strong (s), medium (m) and weak (w). The column normal modes descriptions describes the main atoms displacements involved in the overall molecule vibration. The atom references number are reported in Fig 3 of the main paper. The used abbreviations are reported in the following:  $\nu$ , stretching;  $\nu_s$ , symmetric stretching;  $\nu_a$ , asymmetric stretching; b, bending; w, wagging; sc, scissoring.

adenine	Peak wavenumber		Raman activity	Normal modes description
	Exp.	Sim.		
	1009 (w)	1001	5.9	b(6—NH2) + $\nu$ (1N—6C)
		1058	3.3	w(8C) + b(6—NH2)
	1170 (w)	1218	13.9	b(8—H) + $\nu$ (7N—5C) + $\nu_s$ (1N—2C—3N)
	1252 (w)	1260	3.5	b(8—H) + b(2—H)
		1274	15.2	b(8—H) + b(6—NH2) + $\nu$ (7N—5C)
	1307 (m)	1330	30.2	$\nu_a$ (1N—2C—3N) + $\nu_a$ (2C—1N—6C) + $\nu_a$ (2C—3N—4C)
	1336 (s)	1358	75.5	$\nu_a$ (4C—5C—7N) + b(8—H) + $\nu$ (2C—1N)
	1374 (m)	1363	26.1	$\nu_a$ (7N—8C—9N) + $\nu$ (4C—N) + $\nu$ (2C—1N)
		1391	11.6	b(2—H)
	1421 (m)	1438	7.8	$\nu$ (9N—C) + $\nu$ (4C—9N) + $\nu_s$ (3N—4C—5C)
	1481 (s)	1497	6.5	b(1—H) + $\nu$ (1N—6C) + s c(6—NH2)
	1504 (m)	1532	44.3	$\nu_a$ (7N—8C—9N) + b(8—H) + $\nu_s$ (6C—5C—4C)
	1581 (m)	1607	17.1	sc(6—NH2) + $\nu$ (4C—5C)
	1605 (m)	1621	17.3	$\nu$ (2C—3N) + $\nu$ (1N—6C) + $\nu_s$ (6C—5C—4C)
		1656	8.7	sc(6—NH2) + $\nu$ (6C—N) + $\nu$ (6C—5C)

Guanine	Peak wavenumber		Raman activity	Normal modes description
	Exp.	Sim.		
	1028 (w)	1014	2.9	b(2—NH2) + b(1—H)
	1075 (w)	1050	3.1	$\nu(1N-6C) + \nu(9N-8C) + \nu(2C-N)$
	1189 (w)	1057	4.7	$\nu(1N-6C) + \nu(9N-8C) + b(2-NH2)$
		1083	4.9	b(2—NH2) + $\nu(4C-9N) + b(8-H)$
		1129	3.0	b(2—NH2) + $\nu(2C-3N) + \nu_a(1N-6C-5C)$
		1243	2.8	b(8—H) + $\nu(4C-9N)$
	1323 (m)	1302	1.6	b(8—H) + $\nu_a(5C-7N-8C) + \nu(N3-C5) + \nu(9N-8C)$
	1361 (m)	1333	13.4	b(8—H) + b(1—H) + $\nu(2C-N)$
	1414 (m)	1343	85.1	b(8—H) + $\nu_a(5C-7N-8C) + \nu_a(4C-9N-8C)$
		1387	18.4	b(8—H) + $\nu_s(4C-5C-7N) + \nu(6C-5C) + w(2C)$
	1485 (s)	1507	102.3	$\nu(7N-8C) + \nu(3N-4C)$
	1535 (m)	1564	14.3	$\nu(7N-8C) + \nu(3N-4C) + \nu(1N-2C)$
	1575 (m)	1586	92.1	$\nu(3N-4C) + \nu_s(5C-4C-9N) + \nu_a(1N-2C-3N)$
	1600 (m)	1606	34.1	sc(2—NH2) + $\nu(2C-3N) + b(1-H)$
		1656	37.9	sc(2—NH2) + $\nu(2C-N) + \nu(2C-3N) + b(1-H)$
	1678 (m)	1788	62.0	$\nu(6C-O) + w(6C) + b(6C-O)$

Cytosine	Peak wavenumber		Raman activity	Normal modes description
	Exp.	Sim.		
	951 (w)	947	4.5	$\nu(5C-4C) + \nu(1N-2C) + b(4-NH2)$
	990 (w)	1056	1.6	b(4—NH2) + b(5—H) + $\nu_a(6C-1N-2C)$
		1067	4.2	b(4—NH2) + b(5—H) + $\nu_a(4C-3N-2C)$
	1198 (w)	1161	2.9	b(5—H) + b(6—H) + $\nu(1N-CH3)$
	1250 (m)	1217	18.0	b(5—H) + $\nu(1N-CH3) + \nu(5C-6C)$
	1292 (s)	1248	20.8	$\nu_a(3N-2C-1N) + b(5-H) + \nu(4C-N)$
	1372 (m)	1342	1.6	b(6—H) + $\nu(4C-N)$
		1393	3.8	$\nu(4C-3N) + \nu(1N-2C) + \nu(4C-N) + \nu(1N-C)$
	1472 (m)	1507	5.0	$\nu(4C-N) + \nu(1N-C) + sc(4-NH2)$
		1517	14.5	$\nu(4C-3N) + \nu(4C-N) + sc(4-NH2)$
	1528 (s)	1556	20.6	$\nu(5C-4C) + \nu(5C-6C) + \nu(4C-3N)$
	1563 (m)	1629	9.2	sc(4—NH2) + $\nu(4C-N)$
	1636 (s)	1682	13.7	$\nu_a(5C-6C-1N) + \nu_a(N-4C-3N) + sc(4-NH2)$
		1748	21.8	$\nu(2C-O) + \nu_s(3N-2C-1N)$

Thymine	Peak wavenumber		Raman activity	Normal modes description
	Exp.	Sim.		
1010 (w)		912	2.2	b(6—H)
		1025	5.8	b(5—CH <sub>3</sub> ) + w(6C)
		1067	0.3	b(5—CH <sub>3</sub> ) + v(5C—6C)
1187 (m)	1145	2.1	b(5—CH <sub>3</sub> ) + v <sub>a</sub> (4C—3N—2C) + b(3—H)	
1240 (s)	1196	7.4	v <sub>a</sub> (5C—4C—3N) + b(6—H) + v(1N—2C)	
	1236	6.3	v(5C—H <sub>3</sub> ) + v(3N—2C) + v(5C—4C)	
1374 (s)	1347	10.6	b(6—H) + b(3—H) + v(6C—1N)	
1417 (w)	1387	35.0	b(6—H) + v(1N—R) + v(3N—2C)	
1479 (w)	1413	3.0	b(3—H) b(6—H)	
	1424	12.0	sc(6—CH <sub>3</sub> )	
	1451	5.3	v(5C—4C) + v(1C—2C) + w(5C)	
	1470	8.3	b(6—CH <sub>3</sub> )	
	1499	8.0	sc(6—CH <sub>3</sub> ) + b(6—H)	
1653 (s)	1688	52.6	v(5C—6C) + b(6—H)	
	1749	59.3	v(4C—O) + b(3—H)	
	1772	14.8	v(2C—O) + b(3—H)	

2—hydroxyadenine	Peak wavenumber		Raman activity	Normal modes description
	Exp.	Sim.		
		1072	1.3	w(3N) + b(6—NH <sub>2</sub> ) + v(9N—R)
		1114	3.1	b(6—NH <sub>2</sub> ) + v <sub>s</sub> (OH—2C—3N) + b(2—OH)
		1230	8.7	c + b(8C—H)
		1240	1.3	b(8C—H) + b(2—OH) + v(5C—7N)
1326 (s)	1291	16.0	v(1N—6C) + v(4C—9N) + b(6—NH <sub>2</sub> ) + b(2—OH)	
	1310	15.9	v(5C—7N) + b(8—H) + v(2C—OH)	
	1352	93.2	v(9N—8C) + v(4C—5C) + b(8C—H)	
1417 (m)	1392	36.5	v <sub>a</sub> (2C—1N—6C) + b(2—OH) + v(4C—5C)	
	1421	7.2	v(2C—OH) + v(9N—R) + v <sub>s</sub> (1N—2C—3N)	
	1470	13.5	v(7N—8C) + v(4C—9N) + w(4C)	
1472 (m)	1511	15.7	sc(6—NH <sub>2</sub> ) + v(6C—NH <sub>2</sub> ) + b(2C—OH)	
1506 (m)	1520	4.7	v(6C—NH <sub>2</sub> ) + sc(6—NH <sub>2</sub> ) + b(2C—OH)	
	1546	60.1	b(8C—H) + v(7N—8C) + v(4C—9N)	
1560 (w)	1617	9.9	sc(6—NH <sub>2</sub> ) + v(2C—1N) + v(4C—5C)	
1610 (w)	1639	33.0	v(3N—4C) + v(1N—6C) + w(5C) + sc(6—NH <sub>2</sub> )	
	1661	6.0	v <sub>a</sub> (NH <sub>2</sub> —6C—5C) + sc(6—NH <sub>2</sub> ) + v(2C—3N)	

8—hydroxyadenine	Peak wavenumber		Raman activity	Normal modes description
	Exp.	Sim.		
	1326 (s)	1174	1.3	b(8—OH) + v(8C—OH) + w(7N)
	1417 (m)	1223	9.1	b(8—OH) + v(9N—8C) + b(2C—H)
	1472 (m)	1257	56.6	v(5C—7N) + b(6C—NH <sub>2</sub> )
	1506 (m)	1288	8.4	v(9N—R) + b(8—OH) + b(2C—H) + b(6C—NH <sub>2</sub> )
	1560 (w)	1329	19.7	v <sub>a</sub> (3N—2C—1N) + v <sub>a</sub> (6N—5N—3N)
	1610 (w)	1352	10.9	v(2C—1N) + v(5C—7N) + v <sub>s</sub> (1N—6C—NH <sub>2</sub> )
		1387	3.8	b(2C—H) + v(1N—6C)
		1432	6.5	v(4C—9N) + w(4C)
		1490	5.1	b(2C—H) + w(6C) + b(6C—NH <sub>2</sub> )
		1546	4.9	v(9N—8C) + v(8C—OH) + b(8—OH)
		1582	71.3	sc(6—NH <sub>2</sub> ) + v <sub>a</sub> (7N—8C—OH) + v(6C—5C)
		1613	48.2	v <sub>a</sub> (3N—4C—5C) + sc(6—NH <sub>2</sub> ) + b(2C—H)
		1636	10.7	sc(6—NH <sub>2</sub> ) + v(7N—8C) + v(3N—4C)
		1662	7.2	v <sub>a</sub> (NH <sub>2</sub> —6C—5C) + sc(6—NH <sub>2</sub> )

8—oxoadenine	Peak wavenumber		Raman activity	Normal modes description
	Exp.	Sim.		
	1326 (s)	1083	29.5	v(9N—R) + v(8C—7N) + b(6—NH <sub>2</sub> )
	1417 (m)	1201	8.6	v(9N—8C) + v(2C—3N) + b(6—NH <sub>2</sub> )
	1472 (m)	1272	25.8	v(2C—3N) + v(9N—8C) + v(4C—5C)
	1506 (m)	1280	0.6	v(1N—6C) + b(2—H) + v(9N—R) + b(6—NH <sub>2</sub> )
	1560 (w)	1314	24.3	v(2C—1N) + v(4C—5C)
	1610 (w)	1381	7.0	b(2—H) + v(4C—5C) + b(6—NH <sub>2</sub> )
		1441	9.8	v(5C—7N) + b(2—H)
		1445	39.7	v(5C—7N) + w(5C) + sc(6—NH <sub>2</sub> )
		1503	24.9	sc(6—NH <sub>2</sub> ) + v(6C—NH <sub>2</sub> ) + b(2—H)
		1576	27.5	v(6C—5C) + sc(6—NH <sub>2</sub> ) + v(2C—1N)
		1620	11.3	v <sub>a</sub> (3N—4C—9N) + sc(6—NH <sub>2</sub> ) + w(5C)
		1654	17.9	sc(6—NH <sub>2</sub> ) + v(6C—NH <sub>2</sub> )
		1732	346.9	v(8C—H)

4,6—diamino—5— formamidopyrimidine	Peak wavenumber		Raman activity	Normal modes description
	Exp.	Sim.		
	1326 (s)	1120	8.1	B(9N—H) + b(7—H) + v(3N—4C)
	1417 (m)	1199	1.9	v(9N—R) + v(4C—5C)
	1472 (m)	1207	1.6	v(5C—7N) + b(7—H) + b(6—NH <sub>2</sub> )
	1506 (m)	1250	14.3	v <sub>a</sub> (5C—7N—8C) + b(7—H)
	1560 (w)	1303	15.1	v <sub>a</sub> (6C—5C—4C) + v <sub>a</sub> (1N—2C—3N) + b(6—NH <sub>2</sub> )
	1610 (w)	1349	3.6	b(7—H) + b(8—H) + v <sub>s</sub> (1N—2C—3N)
		1368	4.3	b(2—H) + b(9—H) + v(4C—9N)
		1373	0.9	b(8—H) + b(7—H) + v(5C—7N)
		1420	1.9	b(9—H) + b(2—H) + c
		1454	15.1	b(7—H) + b(8—H) + v(7N—8C)
		1462	19.2	b(9—H) + b(2—H) + b(7—H)
		1485	3.4	b(2—H) + v(6C—NH <sub>2</sub> ) + sc(6—NH <sub>2</sub> )
		1553	5.1	v(4C—9N) + v(2C—1N) + sc(6—NH <sub>2</sub> )
		1608	15.6	v <sub>a</sub> (1N—6C—5C) + v(3N—4C) + v(5C—7N)
		1623	6.4	sc(6—NH <sub>2</sub> ) + b(9—H) v(4C—5C) + v(2C—1N)
		1638	10.3	sc(6—NH <sub>2</sub> ) + v(6C—NH <sub>2</sub> )
		1773	22.2	v(8C—O) + b(8—H) + b(7—H)

8—hydroxyguanine	Peak wavenumber		Raman activity	Normal modes description
	Exp.	Sim.		
	1485 (s)	1083	5.3	b(2—NH <sub>2</sub> ) + v(4C—9N)
	1607 (s)	1132	3.5	v <sub>a</sub> (1N—6C—5C) + b(2—NH <sub>2</sub> ) + b(8—OH)
		1187	6.0	b(8—OH) + v(7N—8C)
		1251	9.0	b(8—OH) + v(9N—8C)
		1296	19.6	v(9N—R) + v(5C—7N) + b(8—OH)
		1334	9.4	b(1—H) + v(2C—NH <sub>2</sub> ) + b(2—NH <sub>2</sub> )
		1387	7.5	v <sub>a</sub> (6C—5C—7N) + v <sub>a</sub> (4C—9N—R) + v <sub>a</sub> (1N—2C—3N)
		1426	22.1	v <sub>a</sub> (5C—4C—9N) + v(1N—2C) + v(9N—R)
		1519	19.6	v(9N—8C) + v(1N—2C)
		1550	30.4	v(8C—OH) + v <sub>a</sub> (4C—9N—8C) + sc(2—NH <sub>2</sub> )
		1589	116.7	v <sub>a</sub> (3N—4C—5C) + v(1N—2C)
		1604	63.7	sc(2—NH <sub>2</sub> ) + v(2C—3N) + b(1—H)
		1628	26.3	v <sub>a</sub> (7N—8C—OH) + v <sub>s</sub> (9N—8C—7N) + v(2C—3N)
		1655	56.1	sc(2—NH <sub>2</sub> ) + v(2C—NH <sub>2</sub> ) + b(1—H)
		1783	61.9	v(6C—O) + v(6C—5C) + b(1—H)

8—oxoguanine	Peak wavenumber		Raman activity	Normal modes description
	Exp.	Sim.		
	1485 (s)	1106	35.9	$\nu(7N-8C) + \nu(9N-R) + b(1-H)$
	1607 (s)	1133	0.8	$\nu(1N-6C) + \nu(2C-3N) + b(2-NH_2)$
		1236	8.3	$\nu(9N-8C) + \nu(9N-R) + b(2-NH_2)$
		1301	23.7	$\nu(5C-4C) + \nu_s(6C-5C-7N) + b(1-H)$
		1352	1.9	$b(1-H) + \nu(2C-NH_2) + b(2-NH_2)$
		1431	39.1	$\nu(9N-R) + \nu(1N-2C) + b(1-H)$
		1472	24.0	$\nu_a(4C-5C-7N) + \nu(9N-R)$
		1547	12.9	$\nu_a(1N-2C-3N) + \nu_a(6C-5C-4C) + b(1-H) + b(2-NH_2)$
		1585	0.6	$sc(2-NH_2) + \nu(2C-3N) + b(1-H)$
		1617	58.1	$\nu_a(3N-4C-9N) + sc(2-NH_2)$
		1660	3.6	$sc(2-NH_2) + \nu(2C-NH_2)$
		1725	376.8	$\nu(8C-O) + w(8C)$
		1772	139.3	$\nu(6C-O) + w(6C) + b(1-H)$

2,6—diamino—4— hydroxy—5— formamidopyrimidine	Peak wavenumber		Raman activity	Normal modes description
	Exp.	Sim.		
	1485 (s)	1150	1.3	$\nu(1N-6C) + \nu(5N-7N) + \nu(2C-3N)$
	1607 (s)	1196	2.0	$b(2-NH_2) + \nu(4C-9N)$
		1207	3.9	$\nu_s(5C-7N-8C) + \nu(9N-R) + \nu(2C-NH_2)$
		1247	10.4	$\nu(7N-8C) + \nu(1N-6C) + \nu_a(4C-9N-R)$
		1310	4.1	$b(1-H) + \nu_a(6C-5C-7N) + b(8-H)$
		1332	3.5	$b(1-H) + \nu(2C-NH_2) + b(2-NH_2)$
		1374	0.8	$b(7-H) + b(8-H)$
		1413	0.6	$b(9-H) + \nu_s(5C-4C-9N)$
		1446	3.4	$b(7-H) + b(8-H) + b(9-H) + w(4C)$
		1461	37.9	$b(7-H) + b(8-H) + b(9-H) + \nu(5C-7N)$
		1521	37.5	$\nu_a(3N-4C-5C) + \nu_s(NH_2-2C-3N)$
		1536	18.7	$b(9-H) + b(1-H) + \nu(1N-2C)$
		1607	14.7	$sc(2-NH_2) + b(1-H) + b(9-H)$
		1638	2.2	$b(9-H) + \nu_a(5C-4C-9N) + \nu_a(1N-2C-3N)$
		1660	21.0	$sc(2-NH_2) + \nu(2C-NH_2) + b(1-H)$
		1747	47.5	$\nu(6C-O) + \nu(6C-5C) + b(1-H)$
		1780	22.6	$\nu(8C-O) + b(8-H) + b(7-H)$

5—hydroxycytosine	Peak wavenumber		Raman activity	Normal modes description
	Exp.	Sim.		
		1081	6.5	$b(4-NH_2) + v(3N-2C)$
		1140	1.4	$b(6-H) + v(6C-1N) + b(5-OH)$
1257 (s)	1202	6.4		$b(5-OH) + v(5C-OH) + b(4-NH_2)$
	1233	35.9		$b(5-OH) + v(3N-2C)$
1385 (w)	1287	5.8		$b(5-OH) + v(4C-NH_2) + v(1N-2C)$
1444 (w)	1310	9.0		$b(6-H) + v(5C-6C)$
	1404	7.7		$v_a(6C-1N-R) + b(5-OH) + b(4-NH_2)$
	1497	1.8		$v_s(5C-4C-3N) + v(4C-NH_2) + b(4-NH_2)$
1547 (m)	1551	25.3		$v_a(5C-4C-3N) + b(4-NH_2)$
$\approx 1650$ (m)	1621	10.2		$sc(4-NH_2) + v(4C-NH_2)$
	1699	15.8		$v(5C-6C) + v(4C-3N) + v(2C-O) + sc(4-NH_2)$
	1747	17.9		$v(2C-O)$

**Fig. S1** Top panel: Raman spectra of a nucleotides solution (at equimolar concentration) compared with the dNTP curve (see main text of the work). Bottom panel: Raman spectra of damaged plasmid DNA without the water contribution (pDNA - ox). The curve dNTP ox and the spectrum of the damaged nucleotide mix solution are still reported for comparison. Vertical dotted lines are guide for the eyes.

