New insights on the Raman and SERS spectra of luteolin under different excitation conditions: experiments and DFT calculations

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Supplementary Information

Table S1. Raman spectrum of luteolin, sample 1 (from Sigma Aldrich): experimental data and proposed assignment based on DFT calculations on the hydrogen bonded conformer (Fig. 2, left panel). Intensity in arbitrary units. The normal mode description expressed as redundant internal coordinates (larger contributions) is provided. The internal coordinates are labeled as follows: first a letter to indicate the nature of the vibration (**s** for stretching, **b** for in plane bending or deformation, **d** for out of plane bending or deformation), then the indication of the atoms and the ring involved (e.g. s CC A indicates a C-C stretching vibration on luteolin ring A).

Calculated				Experimental	
nr.	description	wavenumber	intensity	wavenumber	intensity
77	s CC A b COH A s CC A s CC AC s CC C b CCH C s C=O C	1649	0.39	1658	0.22
75	s CC B s C=O B s CC A	1603	1.00	1613	0.97
74	s CC B b CCH B	1596	0.45	1599	0.97
72	s CC B s CC BC b CCH C s CC A	1568	0.83	1578	0.48
				1570	0.50
71	b CCH B	1521	0.03	1538	0.09
70	b COH A b CCH A s CC A	1494	0.15	1504	0.19
69	b CCH A s CC A s C=O C	1450	0.06	1457	0.23
6	s CC AC s CC A b CCH A b COH A	1382	0.16	1378	0.29
65	b COH B s CC B b CCH C	1356	0.17		
62	s CO B s CC BC s CC B b COH B b CCH B s C-O C	1303	0.35	1315	0.24
				1298	0.92
60	s CO B b CCH B b CCH C	1269	0.06	1267	1.00

59	b CCH C s C-O C s CC C	1251	0.1		
57	b CCH B b CCH C s CC BC	1195	0.34	1219	0.70
55	b CCH B b COH B	1160	0.02	1190	0.05
54	b COH B s CC B	1154	0.02		
52	b COH B b CCH C b CCH B s CC C	1105	0.04	1130	0.12

Table S2. Raman spectrum of luteolin, sample 2 (from Selleck): experimental data and the proposed assignment based on DFT calculations (geometry shown in Fig. 2, right panel). Intensity in arbitrary units. The normal mode description expressed as redundant internal coordinates (larger contributions) is provided. The internal coordinates are labeled as follows: first a letter to indicate the nature of the vibration (**s** for stretching, **b** for in plane bending or deformation, **d** for out of plane bending or deformation), then the indication of the atoms and the ring involved (e.g. s CC A indicates a C-C stretching vibration on luteolin ring A).

Calculated				Experimental	
nr.	description	wavenumber	intensity	wavenumber	intensity
77	s C=O C b CCC C b CCH C s CC C	1663	0.33	1665	0.17
76	s CC C s CC A s CC A b CCH C	1627	0.33	1610	0.37
74	s CC B b CCH B	1606	1.0	1589	1.0
72	s CC A b CCH A s CC C s CC AC b COH A s CC A	1577	0.29		
71	b CCH B	1520	0.03	1506	0.11
70	b CCH A s CC A b COH A	1491	0.02	1492	0.03
69	b CCH A s CC A	1437	0.03	1447	0.24
67	s C-O C s CC AC s C-O A s CC C	1367	0.13	1365	0.08
64	b CCH B b COH B b CCH C s C-O C	1326	0.07	1327	0.05
63	b COH B b CCH C b CCH B s C-O B s CC B	1305	0.13	1303	0.24

62	b CCH B s C-O B b COH B	1291	0.10		
61	s C-O B b CCH B	1266	0.04	1261	0.25
60	b CCH C b CCH A b CCH A	1253	0.07		
58	b COH A b CCH B b CCH C b CCH C	1193	0.15	1223	0.46

Table S3. SERS spectrum of luteolin: experimental data and the proposed assignment based on DFT calculations for the CPLX1 conformer. The experimental bands at ~ 1650 and 1615 cm^{-1} (bold character) do not find a corresponding transition in the calculated spectrum for CPLX1 but are among the most strong features calculated for CPLX2, see Table SI4). Intensity in arbitrary units. The normal mode description in terms of redundant internal coordinates (larger contributions) is provided. The internal coordinates are labeled as follows: first a letter to indicate the nature of the vibration (**s** for stretching, **b** for in plane bending or deformation, **d** for out of plane bending or deformation), then the indication of the atoms and the ring involved (e.g. s CC A indicates a C-C stretching vibration on luteolin ring A).

CPLX1, luteolin-Ag$_{14}$					
Calculated				Experimental	
nr.[1]	description	wavenumber	intensity	514 nm	785nm
83	s CC A b CCH A	1625	0.00	**1652/0.13**	**1649/0.10**
82	s CC B b CCH B	1618	0.03	**1615/0.27**	**1612/0.18**
81	s CC C s CC B b CCH B s CC BC	1589	0.88	1576/0.65	1578/0.41
80	b CCH B s CC B	1584	0.22	1568/0.35	1569/0.45
79	s CC A b CCH A s CC C s CC AC	1553	0.17	1546/0.30	
77	b CCH A s C=O C b COH A	1509	1.00	1509/0.5	1502/0.30
76	s C=O C s CC C s CC A b COH A b CCH A	1488	0.60	1446/0.45	1446/0.10
74	b CCH A s CC A	1416	0.14	1394/0.35	
73	b COH B s CC B	1361	0.07	1363/0.40	1357/0.10
72	b COH B b CCH B	1353	0.18		
69	s C-C BC b COH B s C-O C s CC B	1306	0.43	1308/0.35	1308/0.15
67	s C-O B b CCH B	1289	0.11	1296/0.15	1296/0.15

66	b CCH C	1272	0.19		1253/0.10
65	b CCH A b CCH B	1224	0.24	1220/0.55	1219/0.30
64	b CCH B	1209	0.11		
61	b COH A	1171	0.18		

[1] Please note that the numbering of calculated normal modes for the complex is increased with respect to the corresponding ones of the isolated luteolin due to the six low frequency intermolecular vibrational modes (hindered displacement of the Ag_{14} cluster with respect to the luteolin molecular frame).

Table S4. SERS spectrum of luteolin: experimental data and the proposed assignment based on DFT calculations for the CPLX2 conformer. Intensity in arbitrary units. The normal mode description in terms of redundant internal coordinates (larger contributions) is provided. The internal coordinates are labeled as follows: first a letter to indicate the nature of the vibration (**s** for stretching, **b** for in plane bending or deformation, **d** for out of plane bending or deformation), then the indication of the atoms and the involved (e.g. s CC A indicates a C-C stretching vibration on luteolin ring A).

CPLX2, luteolin-Ag$_{14}$			
Calculated			
nr.[1]	description	wavenumber	intensity
83	s CC C b CCH C s CC BC b OCC BC s C=O C	1649	1.00
81	s CC B b CCH B	1625	0.56
80	s C=O C s CC A s CC B b CCH B	1610	0.26
78	s CC A s C=O C b COH A b CCH A	1586	0.13
77	b CCH B b CCH B b CCH B b CCH B s CC B	1527	0.07
70	b CCH B	1337	0.12
69	b CCH B b COH B	1311	0.07
68	s C-O B s CC C b COH A b CCH B	1290	0.12
67	b CCH C s CC C b CCH A s C-O C	1279	0.12
64	b CCC A b COH A b COH B b CCH B	1196	0.08
continue…			

63	b COH A b COH B s C-O C b CCH B b CCH A	1191	0.06

Table S5. Relevant charge transfer transitions in the near IR- visible spectrum of the luteolin-Ag_{14} CPLX1.

nr.	wavelength / nm	oscillator strength / f
5	1394	0.12
6	1258	0.02
17	549	0.01
18	536	0.01
26	437	0.03
33	407	0.02

Table S6. Relevant charge transfer transitions in the near IR- visible spectrum of the luteolin-Ag_{14} CPLX2.

| nr.	wavelength / nm	oscillator strength f
8	819	0.003
12	601	0.001
22	443	0.001
28	414	0.001
31	400	0.008
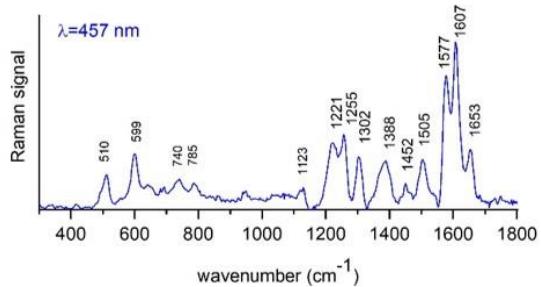
Figure S1. Raman spectrum of luteolin in ethanol (457 nm excitation), as obtained either from Sigma-Aldrich or Selleck suppliers.
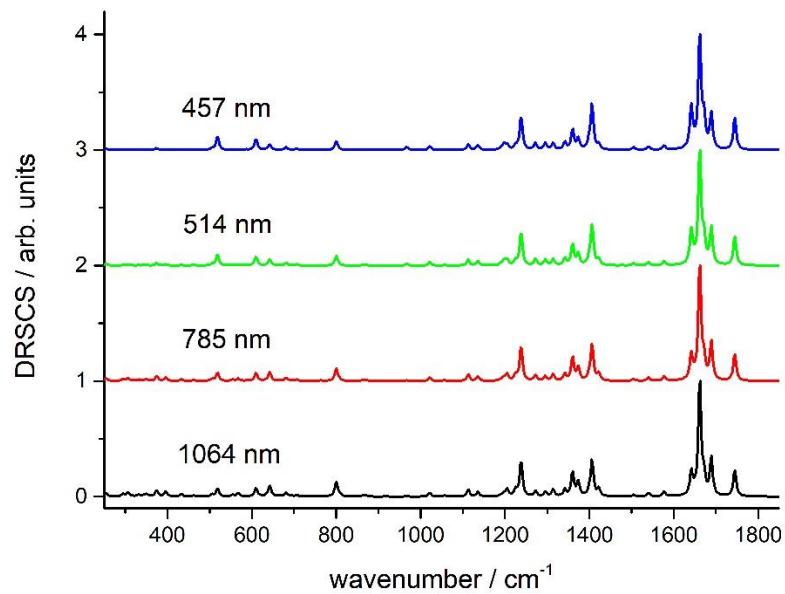

Figure S2. Pre-resonance Raman spectra (DRSCS, frequency unscaled) of luteolin calculated for relevant excitation wavelengths.
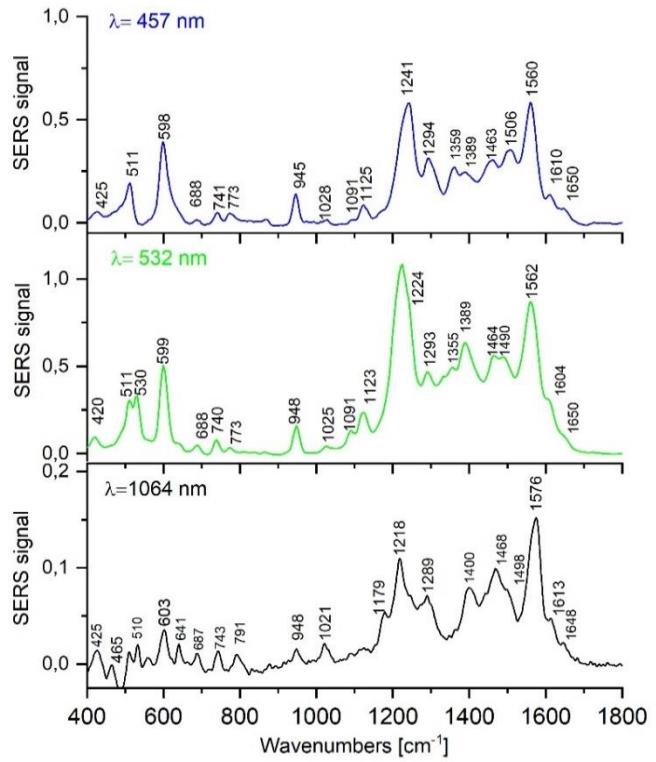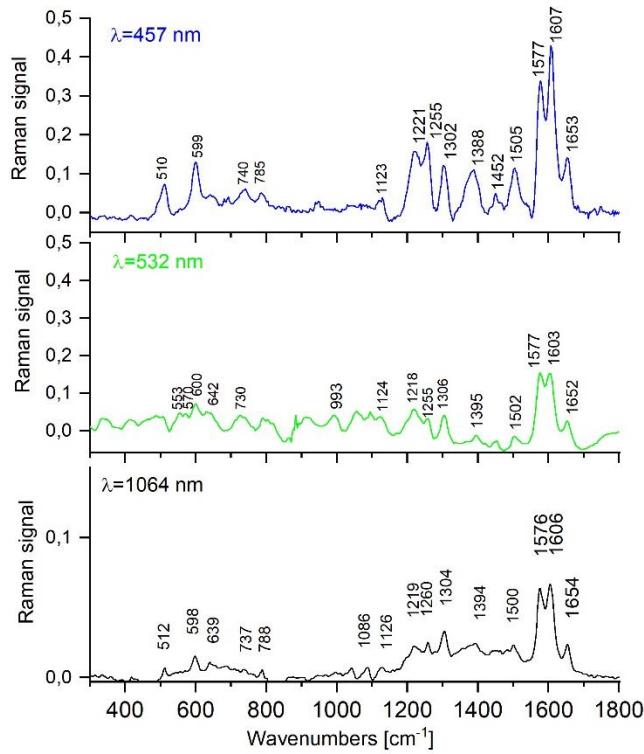
Figure S3. Raman and SERS spectrum of luteolin in solution at different excitation wavelengths