Vibrational and electronic spectra of protonated vanillin: Exploring protonation sites and isomerization

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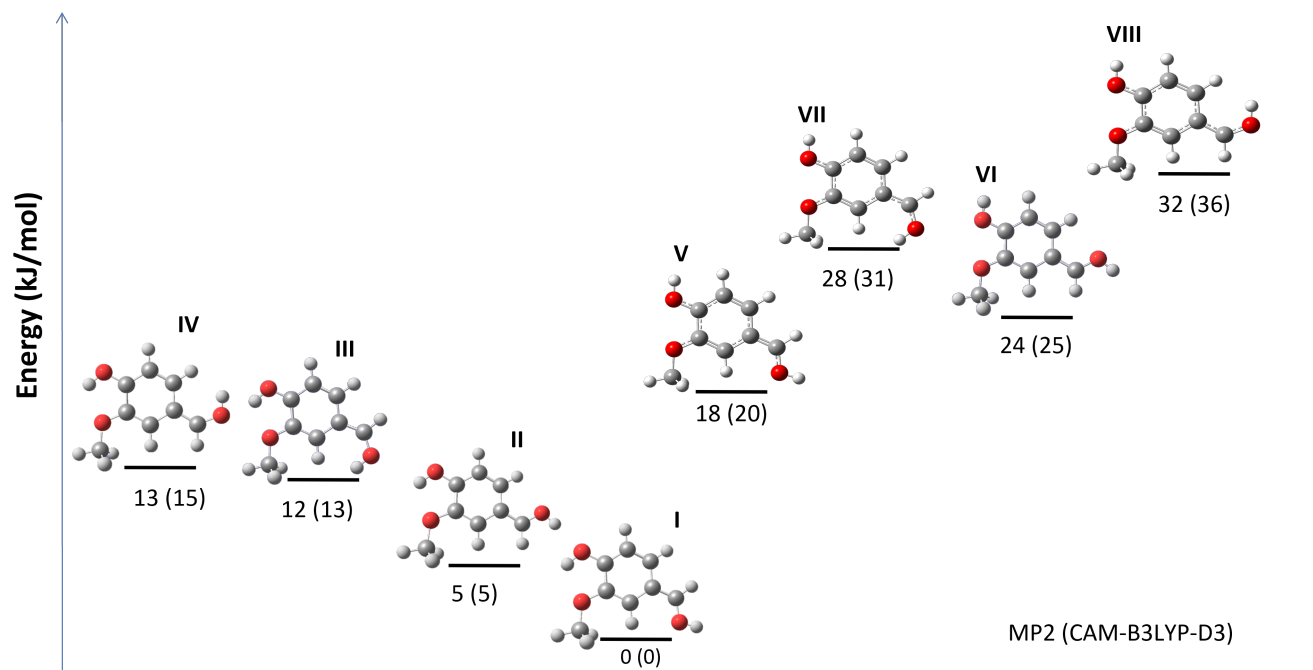
Figure S.1 Relative theoretical energies (kJ/mol) in the ground electronic state for the different vanillin isomers protonated on the carbonyl oxygen ($O_{1'}$) w.r.t. the lowest energy one. Values determined at MP2 and CAM-B3LYP (in parentheses) levels with an aug-cc-pVDZ basis set. The numbering of isomers is based on their relative energies w.r.t. the lowest energy isomer. They are also grouped into two sets: (left) with or (right) without an intramolecular hydrogen bond, to see the influence of such interaction on the relative energies. The other two oxygen protonated species are not shown because the hydroxyl group protonated specie is quite less stable than isomer I (CAM-B3LYP 142 kJ/mol) and the other isomers shown, and the methoxy protonated structure did not even converge to a stable structure despite all the efforts made.
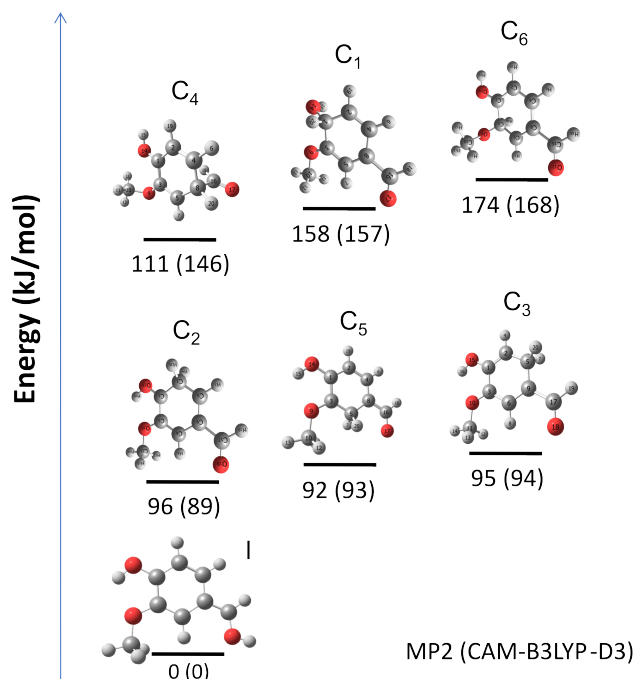

Figure S.2 Relative theoretical energies (kJ/mol) in the ground electronic state for the different vanillin isomers protonated on carbons from the aromatic ring w.r.t. the lowest energy isomer $O_{1'}$ (see carbon atoms numbering in Figure 1 of main document). Values determined at MP2 and CAM-B3LYP (in parentheses) levels with an aug-cc-pVDZ basis set.

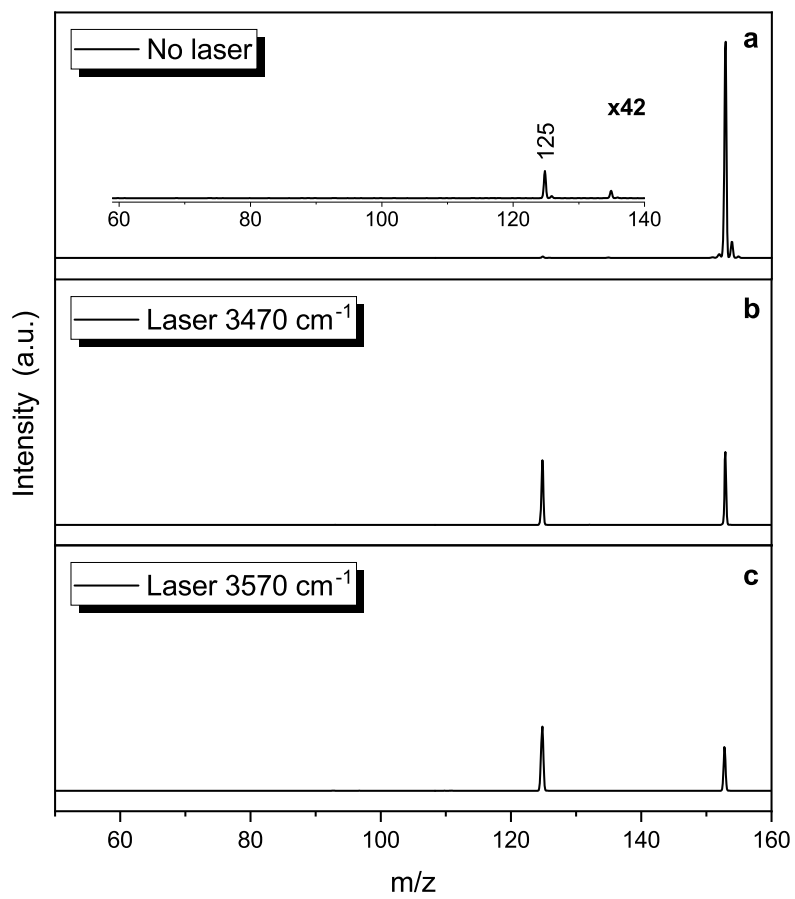Figure S.3 Mass spectra of protonated vanillin under different conditions: (a) isolated vanillin with very low fragmentation energy in the ion trap; IRMPD experiments with IR laser irradiation wavelengths at (b) 3470 cm^{-1} and (c) 3570 cm^{-1}. These data were acquired with the room temperature IRMPD setup at ILM, Lyon. For more details, check the "Methods" section in the main manuscript and references[?][?]

Figure S.4 Comparison of experimental IRMPD spectrum and theoretical infrared spectrum within the harmonic approximation for conformers of vanillin protonated on the oxygen of the carbonyl group. A scaling factor of 0.942 has been applied to theoretical frequencies.

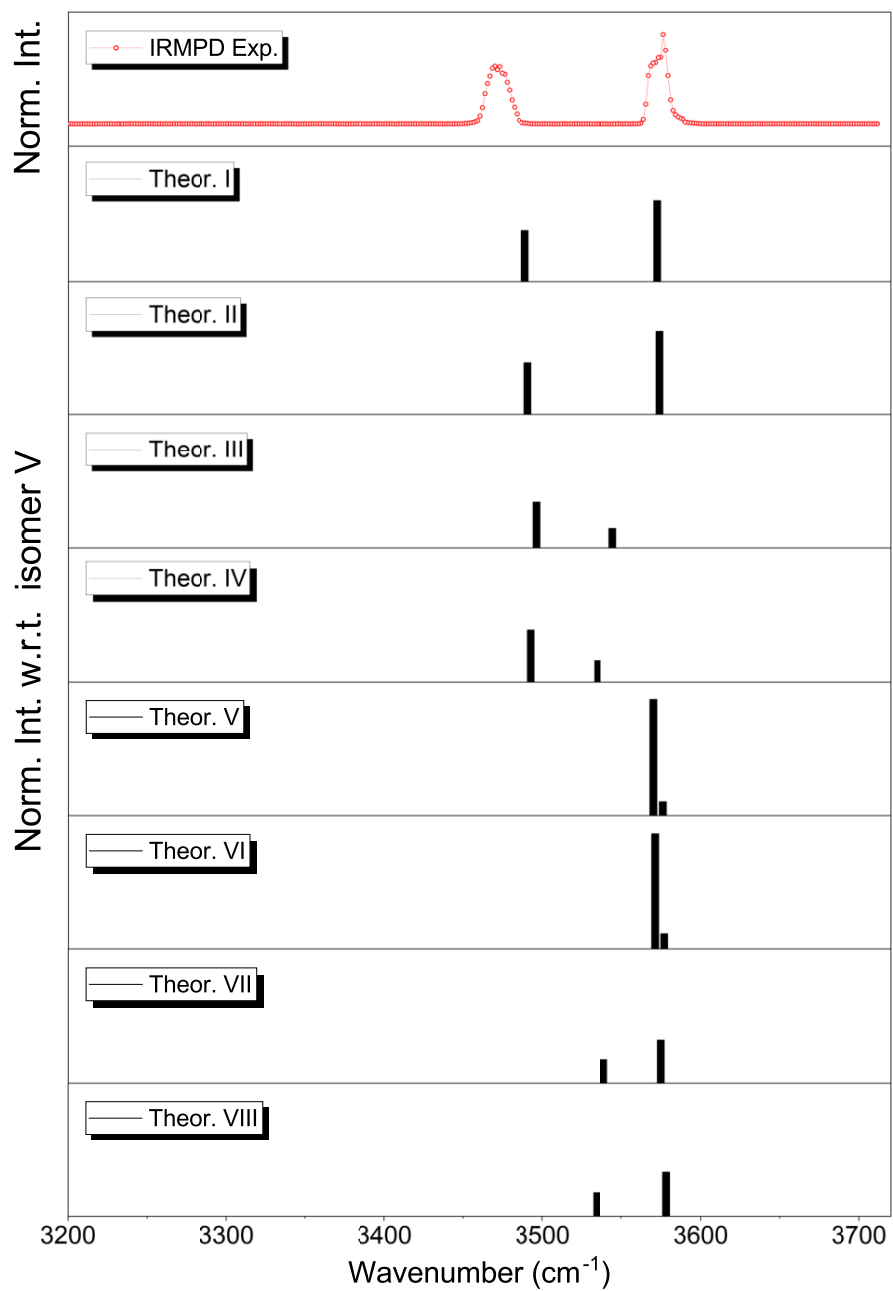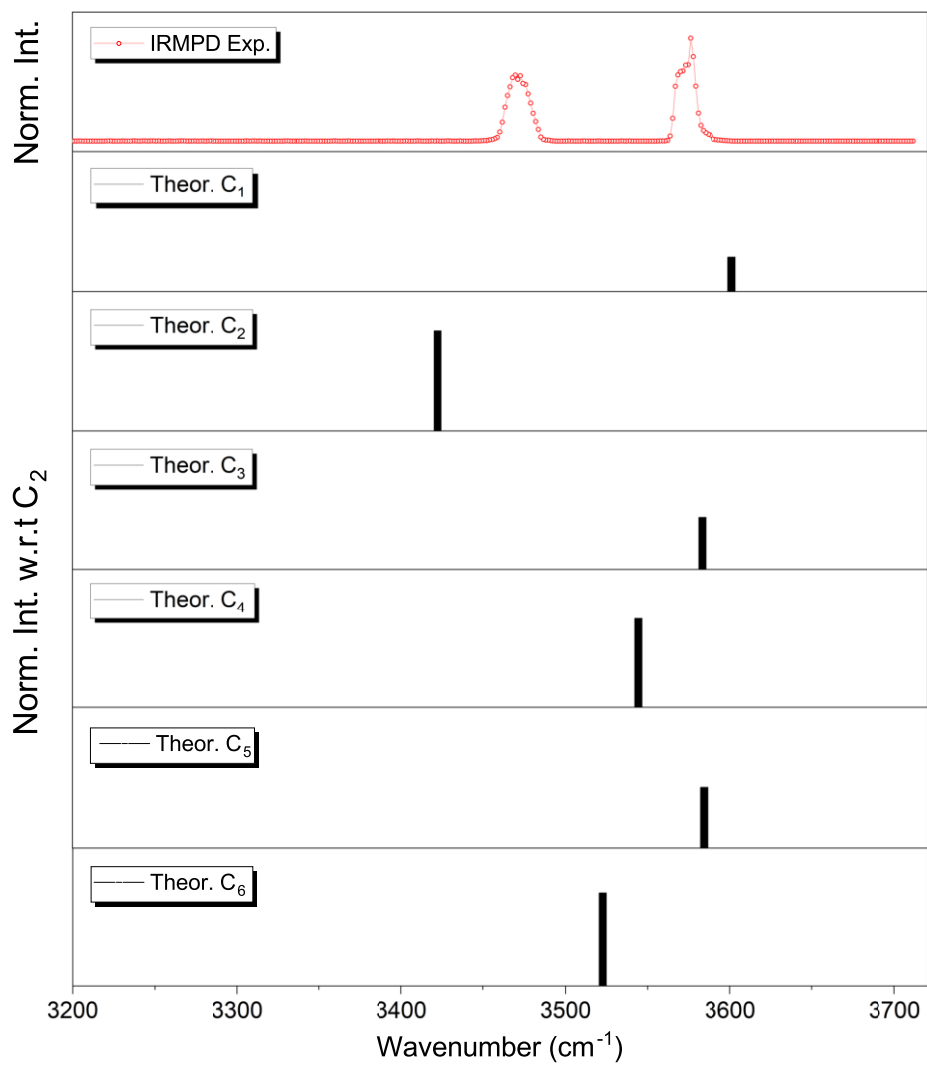Figure S.5 Comparison of experimental IRMPD spectrum and theoretical infrared spectrum within the harmonic approximation for isomers of protonated vanillin on the aromatic ring. A scaling factor of 0.942 has been applied to theoretical frequencies.
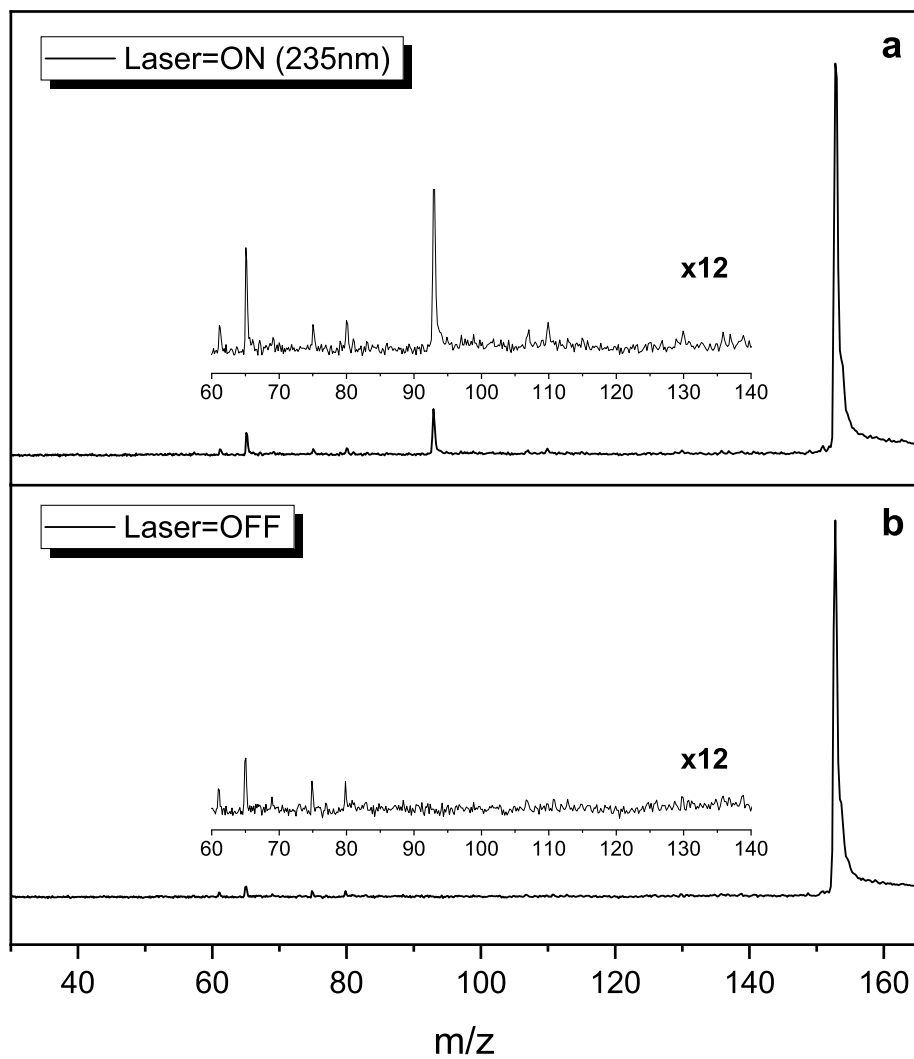
Figure S.6 Time-of-flight (TOF) of protonated vanillin corresponding to the UVPD experiment. The production of ions by UV photoexcitation at 235 nm can be observed by comparison of panels (a) Laser ON and (b) Laser OFF. Mass filters are applied before the ion trap with a mass-gate and inside the ion trap in the form of an additional radiofrequency. Both panels have the same ordinate scale. The m/z=125 corresponding to CO does not appear at this particular irradiation wavelength (235 nm).
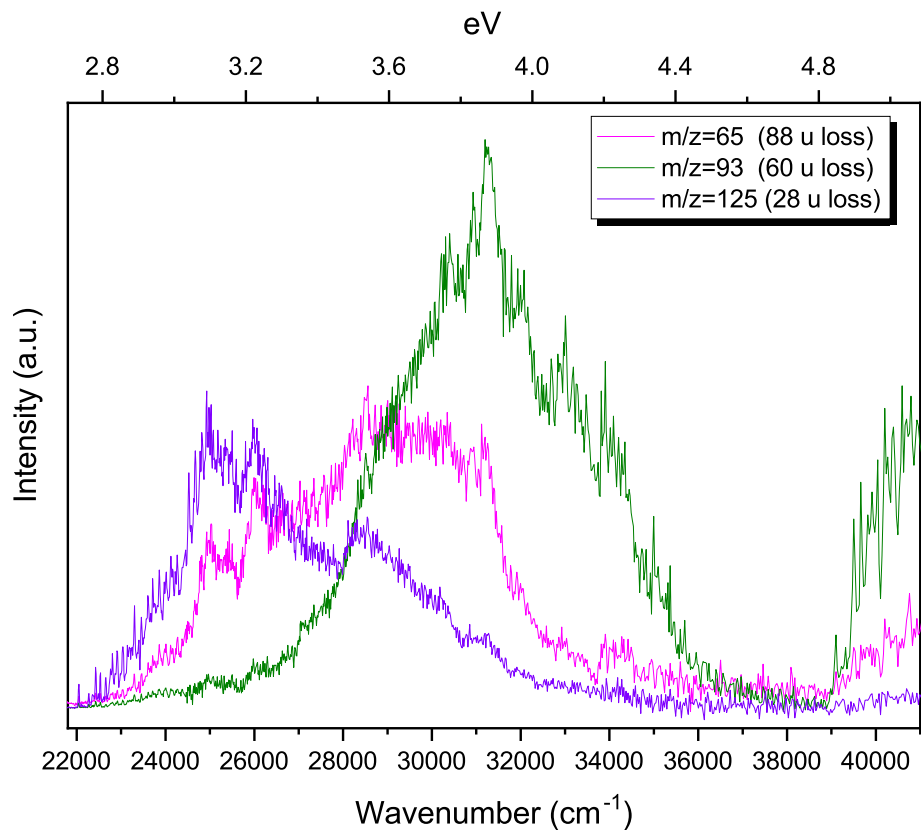
Figure S.7 Photofragmentation spectrum of protonated vanillin recorded at the most intense m/z ratios. The corresponding mass losses with respect to the protonated molecule (m/z=153) are given in the legend.

Vanillin Isom. $O_{1'}$(II)

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Excitation energies and oscillator strengths:

Excited State   1:      Singlet-A'    3.4480 eV  359.58 nm  f=0.1052  <S**2>=0.000
      39 -> 41        0.30315
      40 -> 41        0.63617
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) =  -535.373484242
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State   2:      Singlet-A'    4.2950 eV  288.67 nm  f=0.3898  <S**2>=0.000
      39 -> 41        0.61885
      40 -> 41       -0.29974
      40 -> 42       -0.13533

Excited State   3:      Singlet-A'    5.7962 eV  213.91 nm  f=0.1801  <S**2>=0.000
      39 -> 41        0.12848
      39 -> 46       -0.13529
      40 -> 42        0.66948
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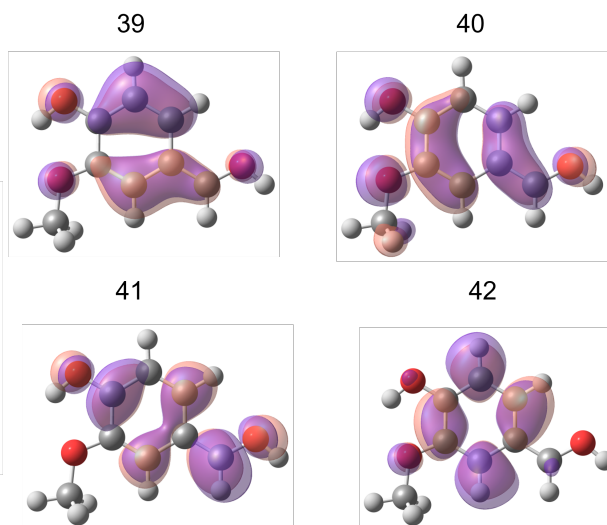

Figure S.8 Molecular orbitals involved in the three first singlet-singlet transitions for the most stable isomer $O_{1'}$ of protonated vanillin.
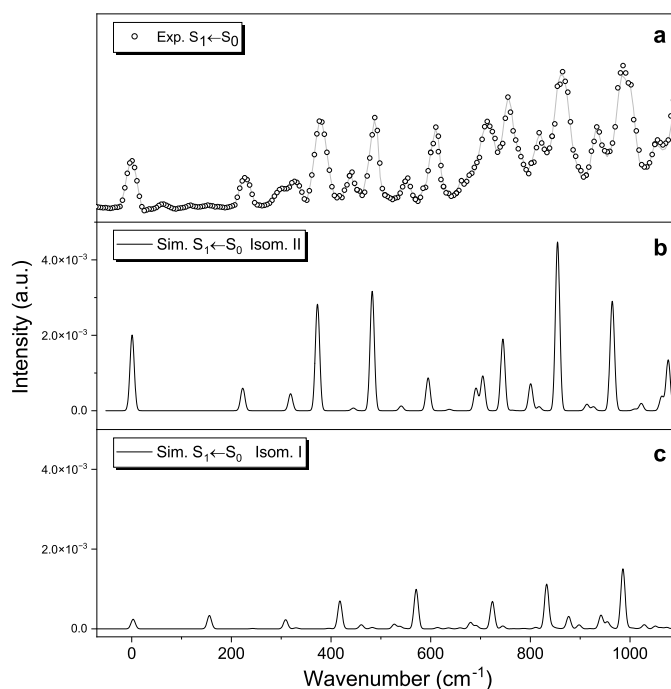
Figure S.9 Origin of the $S_1 \leftarrow S_0$ transition for protonated vanillin. Comparison between (b) Experimental spectrum, and vibronic theoretical transitions (FC factors) simulated with Pgopher for (a) Isomer II and (c) Isomer I. Same graphics as in Figure ??, but using the same scale in pannels b and c, to highlight the difference in FC factor for Isomers I and II.
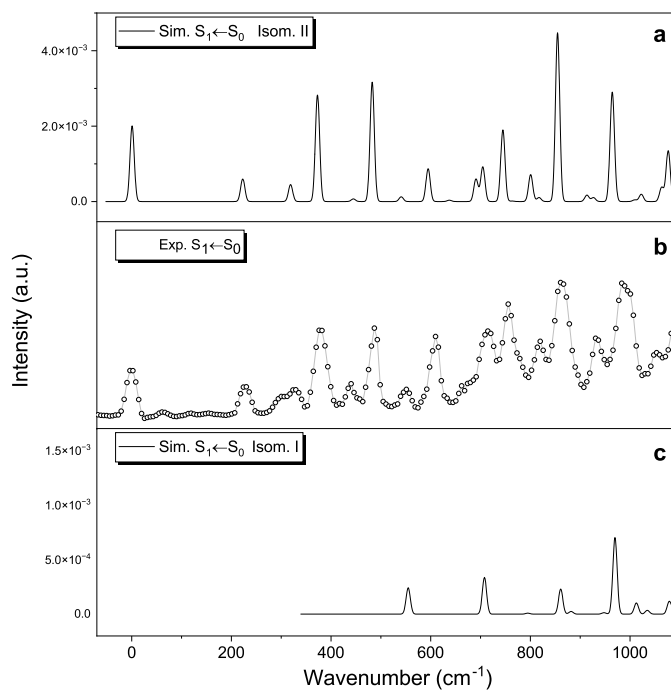
Figure S.10 Origin of the $S_1 \leftarrow S_0$ transition for protonated vanillin. Comparison between (b) Experimental spectrum, and vibronic theoretical transitions (FC factors) simulated with Pgopher for (a) Isomer II and (c) Isomer I. The experimental 0-0 is placed at 22048 cm^{-1} (2.7 eV). The vibronic theoretical transition for isomer I has been shifted 552 cm^{-1}, in agreement with the difference in $S_1 \leftarrow S_0$ adiabatic excitation energy for isomers I and II. Frequency calculations were performed at the CC2/cc-pVDZ theory level.

Figure S.11 Origin of the $S_3 \leftarrow S_0$ transition for protonated vanillin. A baseline correction has been applied.

Table S.1 Ground state energies and excitation energies (AEE: adiabatic, VEE: vertical) for the different isomers of protonated vanillin computed at the CAM-B3LYP/aug-cc-pVDZ level. All the energy values are in eV and are scaled with respect to the ground state of the $O_{1'}(I)$ isomer. Va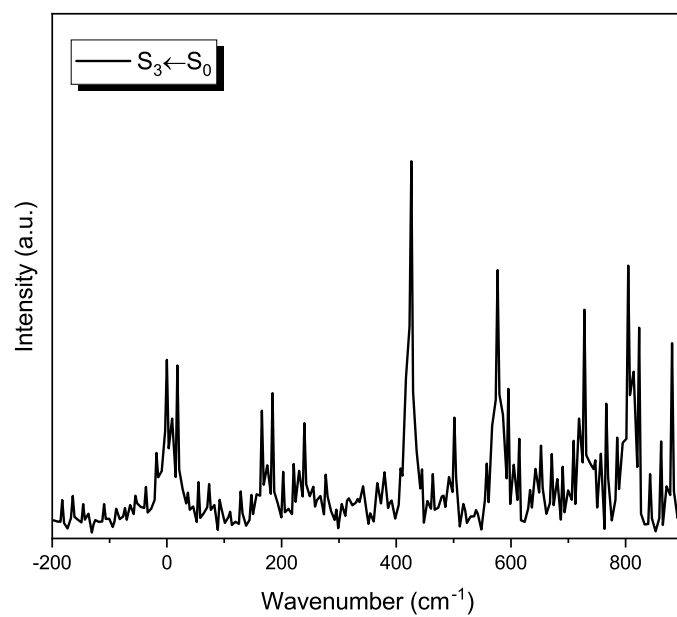lues in italics and parentheses correspond to the oscillator strength of the transition. Only vertical excitations in the 3-6 eV range with non-zero oscillator strength are shown.

			CAM-B3LYP-D3/aug-cc-pVDZ					
	Ground state	AEE		VEE				
$O_{1'}(I)$	0	3.06	3.55 (0.094)	4.24 (0.414)	5.90 (0.134)			
		$S_1 \leftarrow S_0$	$S_1 \leftarrow S_0$	$S_2 \leftarrow S_0$	$S_3 \leftarrow S_0$			
$O_{1'}(II)$	0.05	2.99	3.45 (0.105)	4.30 (0.390)	5.80 (0.180)			
		$S_1 \leftarrow S_0$	$S_1 \leftarrow S_0$	$S_2 \leftarrow S_0$	$S_3 \leftarrow S_0$			
$O_{1'}(III)$	0.13		3.69 (0.121)	4.27 (0.363)	5.87 (0.136)			
			$S_1 \leftarrow S_0$	$S_2 \leftarrow S_0$	$S_3 \leftarrow S_0$			
$O_{1'}(IV)$	0.15		3.49 (0.111)	4.34 (0.347)	5.75 (0.227)			
			$S_1 \leftarrow S_0$	$S_2 \leftarrow S_0$	$S_3 \leftarrow S_0$			
$O_{1'}(V)$	0.21		3.30 (0.090)	4.27 (0.397)	5.76 (0.178)			
			$S_1 \leftarrow S_0$	$S_2 \leftarrow S_0$	$S_3 \leftarrow S_0$			
$O_{1'}(VI)$	0.26		3.20 (0.092)	4.32 (0.370)	5.63 (0.210)			
			$S_1 \leftarrow S_0$	$S_2 \leftarrow S_0$	$S_3 \leftarrow S_0$			
$O_{1'}(VII)$	0.33		3.46 (0.111)	4.31 (0.354)	5.75 (0.179)			
			$S_1 \leftarrow S_0$	$S_2 \leftarrow S_0$	$S_3 \leftarrow S_0$			
$O_{1'}(VIII)$	0.37		3.25 (0.094)	4.36 (0.329)	5.59 (0.265)			
			$S_1 \leftarrow S_0$	$S_2 \leftarrow S_0$	$S_3 \leftarrow S_0$			
C_1	1.63		3.38 (0.103)	4.28 (0.046)	5.03 (0.033)	5.53 (0.053)	5.71 (0.103)	5.96 (0.020)
			$S_2 \leftarrow S_0$	$S_3 \leftarrow S_0$	$S_4 \leftarrow S_0$	$S_5 \leftarrow S_0$	$S_6 \leftarrow S_0$	$S_7 \leftarrow S_0$
C_2	0.93		3.35 (0.122)	5.09 (0.001)	5.61 (0.170)			
			$S_1 \leftarrow S_0$	$S_4 \leftarrow S_0$	$S_5 \leftarrow S_0$			
C_3	0.98		3.55 (0.129)	4.87 (0.142)	5.75 (0.444)			
			$S_2 \leftarrow S_0$	$S_3 \leftarrow S_0$	$S_6 \leftarrow S_0$			
C_4	1.51		3.57 (0.069)	4.17 (0.047)	4.39 (0.076)	4.83 (0.022)	5.37 (0.058)	5.67 (0.228)
			$S_1 \leftarrow S_0$	$S_2 \leftarrow S_0$	$S_3 \leftarrow S_0$	$S_4 \leftarrow S_0$	$S_5 \leftarrow S_0$	$S_6 \leftarrow S_0$
C_5	0.96		3.16 (0.171)	5.18 (0.007)	5.81 (0.432)			
			$S_2 \leftarrow S_0$	$S_4 \leftarrow S_0$	$S_6 \leftarrow S_0$			
C_6	1.75		3.51 (0.022)	3.84 (0.063)	3.92 (0.013)	4.93 (0.008)	5.70 (0.043)	
			$S_2 \leftarrow S_0$	$S_3 \leftarrow S_0$	$S_4 \leftarrow S_0$	$S_5 \leftarrow S_0$	$S_6 \leftarrow S_0$	
Benzaldehyde	-	3.08	3.50 (0.029)					

Table S.2 Optimised structure (Cartesian coordinates) in the ground state (S_0) for isomer II at the CAM-B3LYP/aug-cc-pVDZ level of theory.

	x	y	z
C	-0.831910000000	-1.340053000000	0.000000000000
C	0.471836000000	-1.869519000000	0.000000000000
C	-1.066485000000	0.070407000000	0.000000000000
H	0.590216000000	-2.950769000000	0.000000000000
C	1.541185000000	-1.015821000000	0.000000000000
C	0.000000000000	0.925849000000	0.000000000000
H	2.557163000000	-1.405113000000	0.000000000000
H	-0.148101000000	2.003291000000	0.000000000000
C	1.329707000000	0.393773000000	0.000000000000
O	-2.376193000000	0.383130000000	0.000000000000
C	-2.747197000000	1.764914000000	0.000000000000
H	-2.367347000000	2.260338000000	0.903434000000
H	-2.367347000000	2.260338000000	-0.903434000000
H	-3.838386000000	1.780817000000	0.000000000000
O	-1.851995000000	-2.167249000000	0.000000000000
H	-2.688760000000	-1.668692000000	0.000000000000
C	2.394060000000	1.275994000000	0.000000000000
O	3.629786000000	0.853518000000	0.000000000000
H	2.225498000000	2.357122000000	0.000000000000
H	4.277098000000	1.574210000000	0.000000000000

Table S.3 Optimised structure (Cartesian coordinates) in the first singlet state (S_1) for isomer II at the CAM-B3LYP/aug-cc-pVDZ level of theory.

	x	y	z
C	-0.877010000000	-1.403550000000	0.000000000000
C	0.420094000000	-1.854922000000	0.000000000000
C	-1.080940000000	0.016574000000	0.000001000000
H	0.598684000000	-2.928782000000	-0.000003000000
C	1.509972000000	-0.957088000000	0.000007000000
C	0.026604000000	0.922108000000	0.000002000000
H	2.521101000000	-1.360971000000	0.000007000000
H	-0.167270000000	1.992729000000	0.000001000000
C	1.335372000000	0.437538000000	0.000010000000
O	-2.336426000000	0.399004000000	-0.000002000000
C	-2.727228000000	1.791019000000	0.000000000000
H	-2.350587000000	2.277565000000	0.906558000000
H	-2.350585000000	2.277569000000	-0.906554000000
H	-3.817568000000	1.777655000000	-0.000001000000
O	-1.905855000000	-2.262125000000	-0.000005000000
H	-2.758001000000	-1.805591000000	-0.000005000000
C	2.421852000000	1.360377000000	-0.000001000000
O	3.648164000000	0.843235000000	-0.000002000000
H	2.289116000000	2.439487000000	-0.000006000000
H	4.333341000000	1.524656000000	-0.000009000000

Table S.4 Optimised structure (Cartesian coordinates) in the second singlet state (S_2) for isomer II at the CAM-B3LYP/aug-cc-pVDZ level of theory.

	x	y	z
C	-0.863973000000	-1.342837000000	0.000001000000
C	0.461965000000	-1.853176000000	-0.000002000000
C	-1.092742000000	0.063974000000	0.000002000000
H	0.597256000000	-2.933601000000	-0.000002000000
C	1.565013000000	-0.968756000000	-0.000003000000
C	-0.024009000000	0.924521000000	0.000002000000
H	2.577506000000	-1.362808000000	-0.000005000000
H	-0.177414000000	2.001317000000	0.000003000000
C	1.329864000000	0.410657000000	-0.000002000000
O	-2.398254000000	0.381092000000	0.000000000000
C	-2.768868000000	1.764215000000	-0.000002000000
H	-2.386970000000	2.258166000000	0.903208000000
H	-2.386970000000	2.258164000000	-0.903213000000
H	-3.859999000000	1.779581000000	-0.000003000000
O	-1.868191000000	-2.203059000000	0.000003000000
H	-2.718252000000	-1.725200000000	0.000006000000
C	2.438830000000	1.321457000000	0.000000000000
O	3.653067000000	0.813745000000	-0.000001000000
H	2.310237000000	2.405538000000	0.000005000000
H	4.344733000000	1.493493000000	0.000002000000

Table S.5 Optimised structure (Cartesian coordinates) in the third singlet state (S_3) for isomer II at the CAM-B3LYP/aug-cc-pVDZ level of theory.

	x	y	z
C	-1.040313000000	-1.226118000000	-0.076370000000
C	0.173772000000	-1.989324000000	-0.165550000000
C	-1.056405000000	0.195804000000	-0.169164000000
H	0.127894000000	-3.072384000000	-0.201495000000
C	1.352507000000	-1.256987000000	-0.075411000000
C	0.167442000000	0.915954000000	-0.409156000000
H	2.303485000000	-1.764925000000	0.080831000000
H	0.193111000000	1.923660000000	-0.822014000000
C	1.346641000000	0.160018000000	-0.182483000000
O	-2.207994000000	0.759886000000	0.214656000000
C	-2.388880000000	2.183489000000	0.097514000000
H	-1.664712000000	2.709221000000	0.729568000000
H	-2.282195000000	2.480389000000	-0.953421000000
H	-3.404870000000	2.375918000000	0.445510000000
O	-2.139393000000	-1.882386000000	0.209440000000
H	-2.898949000000	-1.278034000000	0.306780000000
C	2.524152000000	0.936659000000	-0.032315000000
O	3.631074000000	0.383217000000	0.360732000000
H	2.514269000000	2.012840000000	-0.225031000000
H	4.368972000000	1.010599000000	0.438257000000

Table S.6 Ground and excited state normal modes (in cm^{-1}) of the O$_{1'}$(II) isomer of protonated vanillin calculated at the DFT-TDDFT level with the CAM-B3LYP/aug-cc-pVDZ and the CC2/cc-pVDZ levels of theory. The excited state normal mode assignment follows the correspondence with the ground state normal modes in each method.

Symmetry	Mode	S_0 DFT	S_1 TD-DFT	S_0 CC2	S_1 CC2	Symmetry	Mode	S_0 DFT	S_1 TD-DFT	S_0 CC2	S_1 CC2
a' in plane	1	3794	3828	3768	3735	a" out-of-plane	37	3139	3177	3191	3230
	2	3706	3817	3678	3731		38	1485	1483	1494	1487
	3	3247	3239	3266	3247		38	1485	1483	1494	1487
	4	3234	3236	3252	3236		39	1172	1152	1177	1132
	5	3233.5	3229	3251	3226		40	1034	1011	1004	395
	6	3208	3226	3248	3265		41	1021	604	965	940
	7	3181	3242	3202	3212		42	903	887	850	893
	8	3055	3078	3086	3103		43	879	913	810	786
	9	1684	1547	1708	1524		44	793	697	672	858
	10	1671	1595	1676	1680		45	670	548	639	603
	11	1631	1694	1627	1593		46	646	604	630	539
	12	1578	1509	1605	1497		47	573	468	534	474
	13	1509	1483	1543	1395		48	468	432	453	424
	14	1482	1458	1502	1477		49	343	337	328	305
	15	1473	1433	1482	1418		50	316	256	296	218
	16	1462	1406	1472	1450		51	253	198	241	173
	17	1396	1343	1403	1335		52	163	163	155	156
	18	1359	1341	1359	1290		53	103	100	99	68
	19	1346	1306	1351	1299		54	98	104	96	100
	20	1326	1285	1339	1242						
	21	1257	1232	1251	1203						
	22	1229	1207	1229	1199						
	23	1218	1163	1223	1173						
	24	1199	1193	1198	1102						
	25	1161	1134	1145	1122						
	26	1053	1023	1045	974						
	27	956	947	949	894						
	28	832	805	818	774						
	29	769	755	767	721						
	30	632	618	622	595						
	31	558	557	553	545						
	32	518	504	512	482						
	33	410	390	400	372						
	34	344	334	339	318						
	35	246	237	238	222						
	36	172	170	165	158						