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

Electronic Supplementary Information (ESI)

A photoelectron spectroscopic investigation of aspirin, paracetamol and ibuprofen in the gas phase

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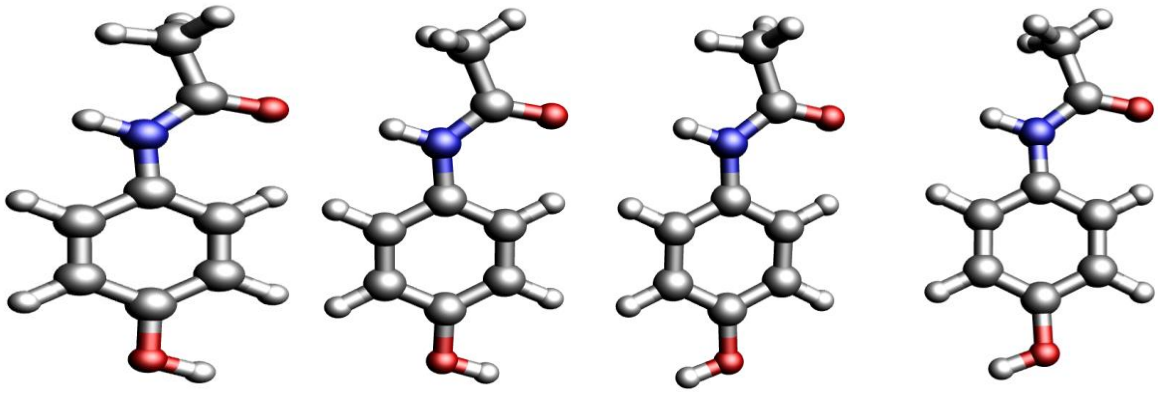
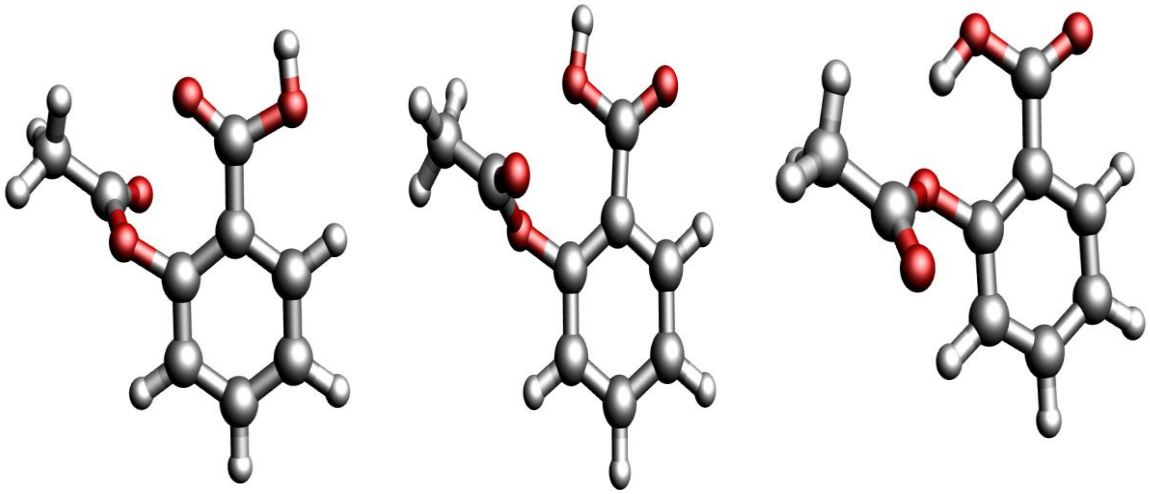
As stated in the main text, the structures found are in agreement with those of Sohn et al. [10] and Varela et al. [11]. As well, structures in which the methyl group is rotated by 60° with respect to one of these conformers were found, namely P2 and P4, Figure S1. Further calculations showed that the barrier for rotation is 0.2 kcal/mol, so that at the temperature of the experiment, the methyl group is rotating freely. Thus, the structures are in full agreement with the results of Varela et al. [11] and Sohn et al. [10].



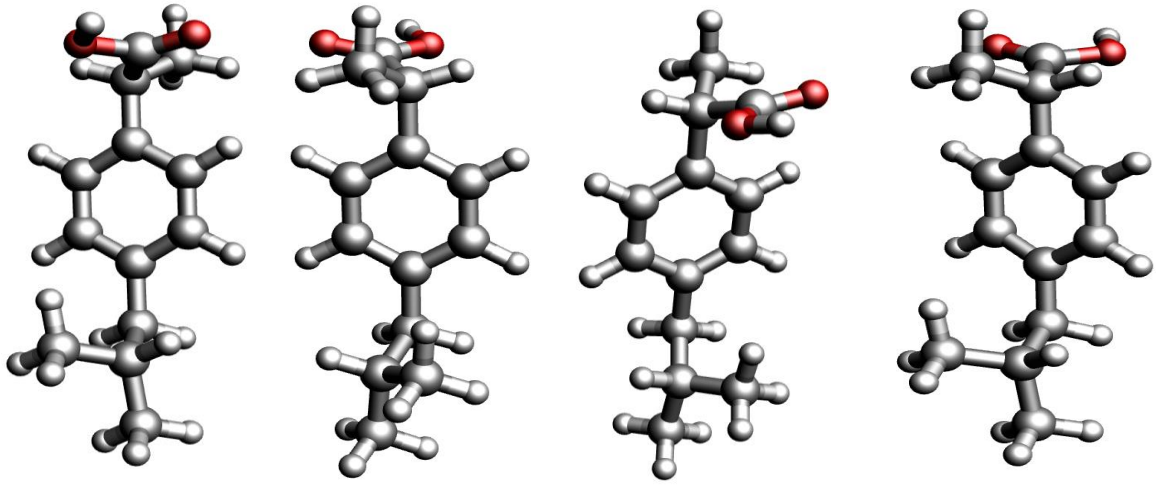
P1 **P2** **P3** **P4**

Figure S1. 3D structures of the four lowest-energy conformers of paracetamol, optimized at the B3PW91/6-311++G(d,p) level of theory. The strain energy cut off is 3.05 kcal/mol. The activatable 3D structural animation of the four paracetamol conformers are included in the PDF file named "Paracetamol_FigureS1", using a technique developed before (https://doi.org/10.1021/jp901678g). Animation can be activated by double clicking the 3D structure in the PDF file.



Aspirin1 **Aspirin2** **Aspirin3**

Figure S2. 3D structures of the three lowest-energy conformers of aspirin, optimized at the B3PW91/6-311++G(d,p) level of theory. The strain energy cut off is 2.55 kcal/mol. The activatable 3D structural animation of the three aspirin conformers are included in the PDF file named "Aspirin_FigureS2", using a technique developed before (https://doi.org/10.1021/jp901678g). Animation can be activated by double clicking the 3D structure in the PDF file.



Ibuprofen1 **Ibuprofen2** **Ibuprofen3** **Ibuprofen4**

Figure S3. 3D structures of the four lowest-energy conformers of ibuprofen, optimized at the B3PW91/6-311++G(d,p) level of theory in the gas phase. The strain energy cut-off is 0.5 kcal/mol. The activatable 3D structural animation of the four ibuprofen conformers are included in the PDF file named "Ibuprofen_FigureS3", using a technique developed before (https://doi.org/10.1021/jp901678g). Animation can be activated by double clicking the 3D structure in the PDF file.

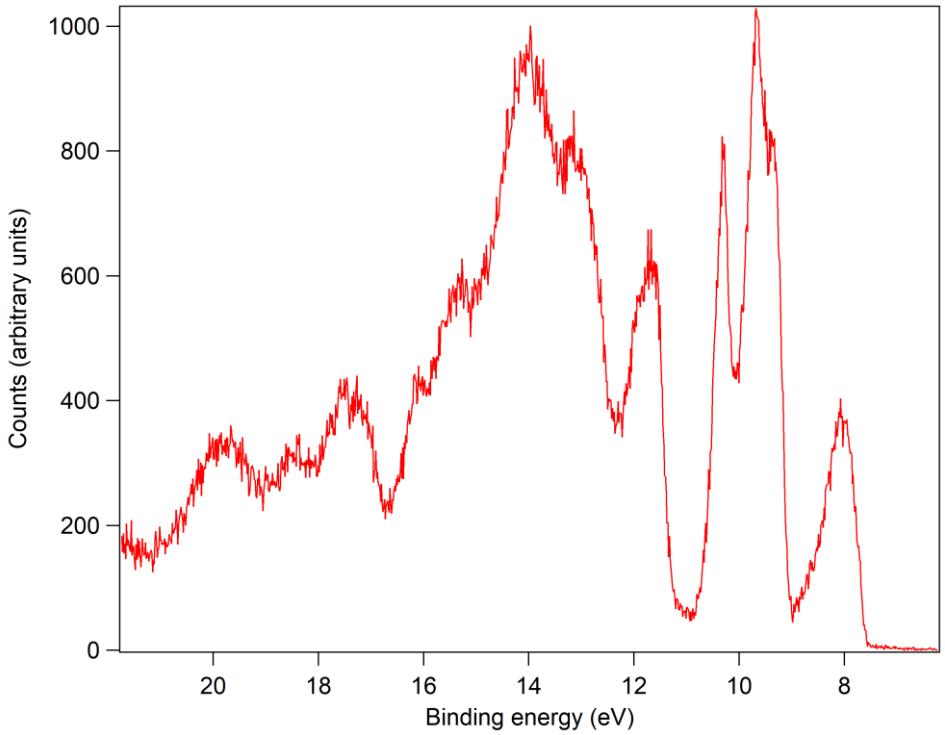


Figure S4. Valence band spectrum of paracetamol. Photon energy: 100 eV.

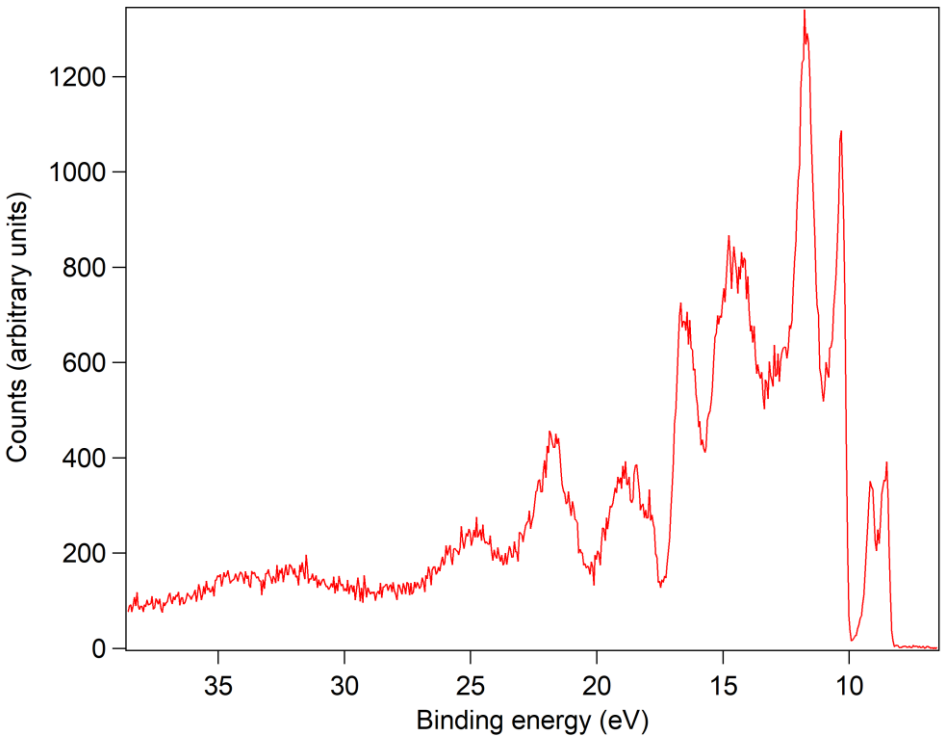


Figure S5. Valence band spectrum of ibuprofen. Photon energy: 100 eV.

Table S1. Theoretical (OVGF) and experimental valence ionization potentials (in eV) of paracetamol. Published values from Novak et al. [3] are also given (in parentheses for experimental results). Spectroscopic pole strengths (PS) are shown for the conformer P1.

P1	PS	P2	P3	P4	Present Experiment (Novak et al.)	Novak et al., theory
7.93	0.9	7.60	7.63	7.60	8.11 (8.05)	7.72
9.24	0.89	9.22	9.23	9.22	9.29, 9.66 (9.35, 9.65)	9.13, 9.76
9.96	0.89	9.99	9.95	9.74	10.33 (10.3)	10.25
10.43	0.87	10.43	10.43	10.43		
12.05	0.85	12.11	12.05	12.11	11.58,11.92 (11.7, 12.0)	11.89, 11.98
12.15	0.89	12.14	12.13	12.11		
13.55	0.88	13.25	13.35	13.34		
13.95	0.9	13.58	13.54	13.57		
14.44	0.89	13.93	13.81	13.82		
14.22	0.84	14.42	14.23	14.19		
14.42	0.88	14.2	14.22	14.2		
14.51	0.88	14.42	14.53	14.5		
15.09	0.87	14.51	14.62	14.63		
15.45	0.87	15.01	15.06	15.05		
15.66	0.87	15.51	15.45	15.5		
16.54	0.85	15.65	15.77	15.77		
18.58	0.05	16.5	16.55	16.53		
18.16	0.86	18.77	17.63	18.3		
		18.12	18.06	18.23		

*The one-particle approximation is not valid for the highlighted IPs.

Table S2. Theoretical (OVGF) and experimental valence ionization potentials (in eV) of ibuprofen. Published values of Novak et al. [3] are also given (in parentheses for experimental results). Spectroscopic pole strengths (PS) are shown for the conformer ibuprofen1.

ibuprofen1	PS	ibuprofen2	ibuprofen3	ibuprofen4	Present Experiment (Novak et al.)	Novak et al., theory
8.35	0.89	8.35	8.34	8.34	8.59 (8.5)	8.26
8.98	0.89	8.98	8.98	8.98	9.14 (9.05)	8.91
10.59	0.89	10.6	10.56	10.59	10.30 (10.35)	10.39
11.38	0.9	11.25	11.42	11.27	(10.75)	11.08
11.41	0.89	11.51	11.43	11.5	(11.8)	11.52
11.47	0.89	11.48	11.41	11.48		
11.81	0.89	11.82	11.77	11.78	11.80	
11.88	0.88	11.85	11.85	11.84		
12.28	0.87	12.01	11.92	12.09		
12.73	0.89	12.2	12.35	12.2	12.80	
13.06	0.9	12.72	12.74	12.7		
13.16	0.9	13.08	12.85	12.9		
13.57	0.91	13.16	13.27	13.26		
13.21	0.89	13.55	13.59	13.6		
14.17	0.9	13.25	13.28	13.3		
14.21	0.88	14.2	14.01	14.03		
14.44	0.88	14.21	14.2	14.21	14.49	
14.63	0.9	14.41	14.64	14.61		
15	0.88	14.62	14.58	14.56		
15.09	0.88	15.02	14.99	15.04		
15.53	0.88	15.08	15.02	15.01		
15.63	0.87	15.09	15.14	15.14		
16.58	0.87	15.52	15.34	15.34		
16.76	0.87	15.64	15.83	15.84		
17.16	0.89	16.58	16.5	16.5	16.57	
		16.76	16.78	16.78		
		17.16	17.17	17.17		
					18.27	
					19.42	
					20.90	
					22.01	

Table S3. Comparison of theoretical and experimental valence ionization potentials (in eV) of salicylic acid.

Orbitals	**Theory**		**Experiment**		
	Hill[a] [31]	Novak et al.[b] [3]	Tseplin et al. [30]	Novak et al. [3]	Hill [31]
6a'' (HOMO)	8.64	8.55	8.87	8.8	8.81
5a''	9.41	9.38	9.78	9.65	9.75
30a'	11.08	10.95	10.82	10.75	10.73
29a'	11.96*	11.7	11.76	11.8	11.96
4a''	12.29	12.1	12.07	12.0	11.96
3a''	12.45	12.31	12.38	12.1	11.96
28a'	13.26		13.06	13.1	13.31
27a'	13.91		13.55	13.4	14.06
26a'	14.22		13.98	13.9	
2a''	14.43		14.22	14.1	14.73
25a'	15.08		14.79	14.75	15.54
24a'	15.76		15.30	15.2	
23a'	15.85		-	15.4	
1a''	16.12			15.55	16.88
22a'	17.53				17.50
21a'	17.56				
20a'	18.06				
					19.07
					19.67
					21.13
					23.04

[a] OVGF/6-311++G(d, p) level.
[b] OVGF 6-311G(d,p).
*The spectroscopic pole strength of 29a' is 0.849.