

SUPPLEMENTARY MATERIAL

Comparison between QM (AM1) and QM/MM Mulliken charges.

S1

Comparison between AM1, LSCF, HQ and QQ values of the Mulliken charges for the two positions of the boundary for the propanol with a sodium ion (position 4).

	AM1	LSCF Cut1	LSCF Cut2	HQ Cut 1	HQ Cut 2	QQ Cut 1	QQ Cut 2
Link atom					0.07		0.37
C <sup>2</sup>	-0.16		-0.21		-0.21		-0.50
H <sup>21</sup>	0.07		0.08		0.06		0.06
H <sup>22</sup>	0.07		0.08		0.06		0.06
Link atom				0.06		0.33	
C <sup>3</sup>	-0.01	-0.07	0.01	-0.06	-0.01	-0.32	0.01
H <sup>31</sup>	0.07	0.09	0.07	0.06	0.07	0.06	0.06
H <sup>32</sup>	0.07	0.09	0.07	0.06	0.07	0.06	0.06
O	-0.34	-0.34	-0.33	-0.34	-0.34	-0.33	-0.34
H	0.22	0.23	0.22	0.22	0.22	0.21	0.21

S2

Comparison between AM1, LSCF, HQ and QQ values of the Mulliken charges for the two positions of the boundary for the acid form of propanol with a sodium ion (position 4).

	AM1	LSCF cut1	LSCF cut2	HQ cut 1	HQ cut 2	QQ cut 1	QQ cut 2
Link atom					0.15		0.43
C <sup>2</sup>	-0.18		-0.16		-0.24		-0.51
H <sup>21</sup>	0.10		0.11		0.09		0.09
H <sup>22</sup>	0.06		0.11		0.09		0.09
Link atom				0.15		0.40	
C <sup>3</sup>	-0.07	-0.04	-0.06	-0.12	-0.07	-0.37	-0.05
H <sup>31</sup>	0.16	0.19	0.17	0.16	0.17	0.16	0.16
H <sup>32</sup>	0.16	0.19	0.17	0.16	0.17	0.16	0.16
O	-0.09	-0.10	-0.08	0.09	-0.09	-0.07	-0.09
H	0.36	0.38	0.37	0.36	0.36	0.36	0.36
H	0.36	0.38	0.37	0.36	0.36	0.36	0.36

S3

Comparison between AM1, LSCF and HQ Mulliken charges for propanol, propanolate and the acid form summed by group (cf. Fig.3) with a sodium ion (position 2).

	C <sup>1</sup> H <sub>3</sub>		C <sup>2</sup> H <sub>2</sub>		C <sup>3</sup> H <sub>2</sub>		OH/O <sup>-</sup> /OH <sub>2</sub> <sup>+</sup>		
	AM1	LSCF <sup>a</sup>	AM1	LSCF	AM1	LSCF	AM1	LSCF	HQ
Propanol	-0.04	0.00	0.05	-0.01	0.10	0.11	-0.11	-0.10	-0.11
Propanoate	-0.14	0.00	-0.05	-0.19	-0.02	-0.02	-0.79	-0.79	-0.80
Oxonium ion	0.06	0.00	0.08	0.09	0.22	0.24	0.64	0.67	0.64

S4

Comparison between AM1, LSCF and HQ Mulliken charges for propanol, propanolate and the acid form summed by group (cf. Fig.3) with a sodium ion (position 4).

	C <sup>1</sup> H <sub>3</sub>		C <sup>2</sup> H <sub>2</sub>		C <sup>3</sup> H <sub>2</sub>		OH/O <sup>-</sup> /OH <sub>2</sub> <sup>+</sup>		
	AM1	LSCF <sup>a</sup>	AM1	LSCF	AM1	LSCF	AM1	LSCF	HQ
Propanol	0.01	0.00	-0.02	-0.05	0.13	0.15	-0.12	-0.11	-0.12
Propanoate	-0.11	0.00	-0.13	-0.23	0.03	0.03	-0.79	-0.80	-0.80
Oxonium ion	0.13	0.00	-0.03	0.06	0.26	0.28	0.64	0.66	0.64

## S5

Comparison between AM1, LSCF and HQ Mulliken charges for propanol, propanoate and the acid form summed by group (cf. Fig.3) with a sodium ion (position 3).

	C <sup>1</sup> H <sub>3</sub>		C <sup>2</sup> H <sub>2</sub>		C <sup>3</sup> H <sub>2</sub>		OH/O/OH <sub>2</sub> <sup>+</sup>		
	AM1	LSCF <sup>a</sup>	AM1	LSCF	AM1	LSCF	AM1	LSCF	HQ
Propanol	0.02	0.00	0.07	0.06	0.02	0.03	-0.10	-0.09	-0.10
Propanoate	-0.09	0.00	-0.02	-0.12	-0.11	-0.11	-0.78	-0.77	-0.78
Oxonium ion	-0.02	0.00	0.11	0.16	0.27	0.17	0.64	0.68	0.64

## S6

Comparison between AM1, LSCF and HQ Mulliken charges for propanol, propanoate and the acid form summed by group (cf. Fig.3) with a sodium ion (position 6).

	C <sup>1</sup> H <sub>3</sub>		C <sup>2</sup> H <sub>2</sub>		C <sup>3</sup> H <sub>2</sub>		OH/O/OH <sub>2</sub> <sup>+</sup>		
	AM1	LSCF <sup>a</sup>	AM1	LSCF	AM1	LSCF	AM1	LSCF	HQ
Propanol	0.04	0.00	0.03	0.04	0.12	0.13	-0.19	-0.17	-0.19
Propanoate	-0.07	0.00	-0.06	-0.13	0.01	0.02	-0.89	-0.88	-0.89
Oxonium ion	0.14	0.00	0.21	0.14	0.23	0.25	0.56	0.61	0.56

(a) Classical charges are set to zero for C<sup>1</sup>H<sub>3</sub> in the QM/MM computations.

S7

Cartesian coordinates of the structure used for propanol and the acidic and basic form.

Propanol			
C <sup>1</sup>	0.76436	-0.00995	0.00000
H <sup>11</sup>	1.13190	-1.05292	0.00000
H <sup>12</sup>	1.19298	0.48455	-0.89199
H <sup>13</sup>	1.19298	0.48455	0.89199
C <sup>2</sup>	-0.76981	0.03885	0.00000
H <sup>21</sup>	-1.16576	-0.50297	0.88085
H <sup>22</sup>	-1.16576	-0.50297	-0.88085
LA	-0.92000	0.45000	0.00000
C <sup>3</sup>	-1.30185	1.47317	0.00000
H <sup>31</sup>	-0.93811	2.02548	0.88922
H <sup>32</sup>	-0.93811	2.02548	-0.88922
O	-2.72450	1.42735	0.00000
H <sup>1</sup>	-3.05000	1.89000	0.82000
H <sup>2</sup>	-3.05000	1.89000	-0.82000

  

Ion			
Na <sup>1</sup>	3.50000	0.00000	0.00000
Na <sup>2</sup>	5.50000	0.00000	0.00000
Na <sup>3</sup>	0.00000	5.00000	0.00000
Na <sup>4</sup>	0.00000	-4.00000	0.00000
Na <sup>5</sup>	-4.00000	4.92000	0.00000
Na <sup>6</sup>	-5.97550	3.48400	0.00000