

# On the pK of crystal surfaces: molecular modelling of crystallite protonation, local reorganization, and solute dissociation

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## Supporting Information

The atomic partial charges were obtained following the two-step restricted electrostatic potential (RESP) method explained in the simulation details part by Gadelmeier et al.. The charges of the charged carbamazepine species were generated in analogous manner, while charge shift was restricted to atoms N<sub>25</sub> to H<sub>31</sub>.

Table S1 Atomic partial charges. Parameters using the notation of atoms as in Fig.1.

Atom	Charge / e CBZ	Charge / e CBZH+	Atom	Charge / e CBZ	Charge / e CBZH+
C <sub>1</sub>	-0.144727	"	C <sub>16</sub>	0.169333	"
H <sub>2</sub>	0.150322	"	C <sub>17</sub>	-0.242432	"
C <sub>3</sub>	-0.15251	"	H <sub>18</sub>	0.164999	"
H <sub>4</sub>	0.150956	"	C <sub>19</sub>	-0.144727	"
C <sub>5</sub>	-0.242432	"	H <sub>20</sub>	0.150322	"
H <sub>6</sub>	0.164999	"	C <sub>21</sub>	-0.15251	"
C <sub>7</sub>	0.158977	"	H <sub>22</sub>	0.150956	"
C <sub>8</sub>	0.169333	"	C <sub>23</sub>	-0.205923	"
C <sub>9</sub>	-0.205923	"	H <sub>24</sub>	0.173583	"
H <sub>10</sub>	0.173583	"	N <sub>25</sub>	-0.370568	-0.057925
C <sub>11</sub>	-0.232443	"	C <sub>26</sub>	0.848475	0.855558
H <sub>12</sub>	0.151156	"	O <sub>27</sub>	-0.599942	-0.540213
C <sub>13</sub>	-0.232443	"	N <sub>28</sub>	-0.922229	-0.917324
H <sub>14</sub>	0.151156	"	H <sub>29</sub>	0.380842	0.441120
C <sub>15</sub>	0.158977	"	H <sub>30</sub>	0.380842	0.441120
			H <sub>31</sub>	-	0.495070

The bond description employed is a harmonic potential, which is implemented in LAMMPS as

$$E_{bond} = K * (r - r_0)^2$$

where  $r_0$  is the equilibrium bond distance. The angle term employed is a harmonic potential given in LAMMPS by

$$E_{angle} = K * (\delta - \delta_0)^2$$

where  $\delta_0$  is the equilibrium value of the angle. The dihedral terms employed in LAMMPS with the following term by

$$E_{dihedral} = K * [1 + \cos(n\phi - d)]$$

Table S2 Newly added intramolecular force-field parameters for modGAFF. Parameters using the notation of atoms as in Fig.1.

Bonds	K / eV	$r_0 / \text{\AA}$	
C <sub>7</sub> -C <sub>11</sub>	17.699516	1.4614	
C <sub>7</sub> -C <sub>8</sub>	26.995188	1.3961	
C <sub>8</sub> -N <sub>25</sub>	20.660489	1.4231	
C <sub>11</sub> -C <sub>13</sub>	31.000000	1.3373	
C <sub>13</sub> -C <sub>15</sub>	17.699516	1.4614	
C <sub>15</sub> -C <sub>16</sub>	19.995188	1.3961	
N <sub>25</sub> -O <sub>26</sub>	15.542491	1.3878	
C <sub>26</sub> -N <sub>28</sub>	20.542491	1.3938	
Angles	K / eV	$\delta_0 / ^\circ$	
C <sub>7</sub> -C <sub>11</sub> -C <sub>13</sub>	2.431413	127.7251	
C <sub>8</sub> -N <sub>25</sub> -C <sub>16</sub>	1.509994	117.5021	
C <sub>8</sub> -N <sub>25</sub> -C <sub>26</sub>	1.509994	117.5000	
N <sub>25</sub> -C <sub>26</sub> -O <sub>27</sub>	3.717617	122.3830	
Dihedral	K / eV	n	d / °
C <sub>8</sub> -C <sub>7</sub> -C <sub>11</sub> -C <sub>13</sub>	0.030355	2	180
N <sub>25</sub> -C <sub>26</sub> -N <sub>28</sub> -H <sub>30</sub>	0.021025	2	0

The following changes in interaction description occur upon protonation of the neutral species carbamazepine.

Table S3. Changes in molecular description upon protonation of CBZ to CBZH+. Parameters using the notation of atoms as in Fig.1.

Pair	$\varepsilon$ / eV	$\sigma$ / Å	
O <sub>27</sub>	0.009124	3.066473	
H <sub>31</sub>	0.000650	2.599642	
Bonds	K / eV	$r_0$ / Å	
N <sub>25</sub> -C <sub>26</sub>	15.542500	1.3164	
C <sub>26</sub> -O <sub>27</sub>	18.108900	1.3083	
N <sub>28</sub> -H <sub>29</sub>	17.484400	1.0070	
N <sub>28</sub> -H <sub>30</sub>	17.484400	1.0070	
O <sub>27</sub> -H <sub>31</sub>	16.105400	0.9611	
Angles	K / eV	$\delta_0$ / °	
N <sub>25</sub> -C <sub>26</sub> -O <sub>27</sub>	3.717620	116.7460	
N <sub>25</sub> -C <sub>26</sub> -N <sub>28</sub>	3.161240	121.8260	
C <sub>26</sub> -N <sub>28</sub> -H <sub>29</sub>	1.894490	120.5030	
C <sub>26</sub> -N <sub>28</sub> -H <sub>30</sub>	1.894490	120.5030	
O <sub>27</sub> -C <sub>26</sub> -N <sub>28</sub>	3.017620	123.0000	
H <sub>29</sub> -N <sub>28</sub> -H <sub>30</sub>	1.117220	118.4810	
C <sub>26</sub> -O <sub>27</sub> -H <sub>31</sub>	2.000000	113.7940	
Dihedral	K / eV	n	d / °
C <sub>8</sub> -N <sub>25</sub> -C <sub>26</sub> -O <sub>27</sub>	0.128075	2	180
C <sub>8</sub> -N <sub>25</sub> -C <sub>26</sub> -N <sub>28</sub>	0.128075	2	180
C <sub>16</sub> -N <sub>25</sub> -C <sub>26</sub> -O <sub>27</sub>	0.128075	2	180
C <sub>16</sub> -N <sub>25</sub> -C <sub>26</sub> -N <sub>28</sub>	0.128075	2	180
N <sub>25</sub> -C <sub>26</sub> -N <sub>28</sub> -H <sub>30</sub>	0.077500	2	180
O <sub>27</sub> -C <sub>26</sub> -N <sub>28</sub> -H <sub>29</sub>	0.077500	2	180
N <sub>25</sub> -C <sub>26</sub> -O <sub>27</sub> -H <sub>31</sub>	0.111383	2	180
N <sub>28</sub> -C <sub>26</sub> -O <sub>27</sub> -H <sub>31</sub>	0.245532	2	180

The following changes in interaction description occur upon protonation of the neutral species carbamazepine.

The following statistic shows the distribution of computed pKa values as observed for the calcite model featuring the screw-like crystallite. Here, negative pKa refers to particularly unfavorable protonation energy, whereas only protonation of sites with pKa > 3 and pKa > 4 were explored in detail.

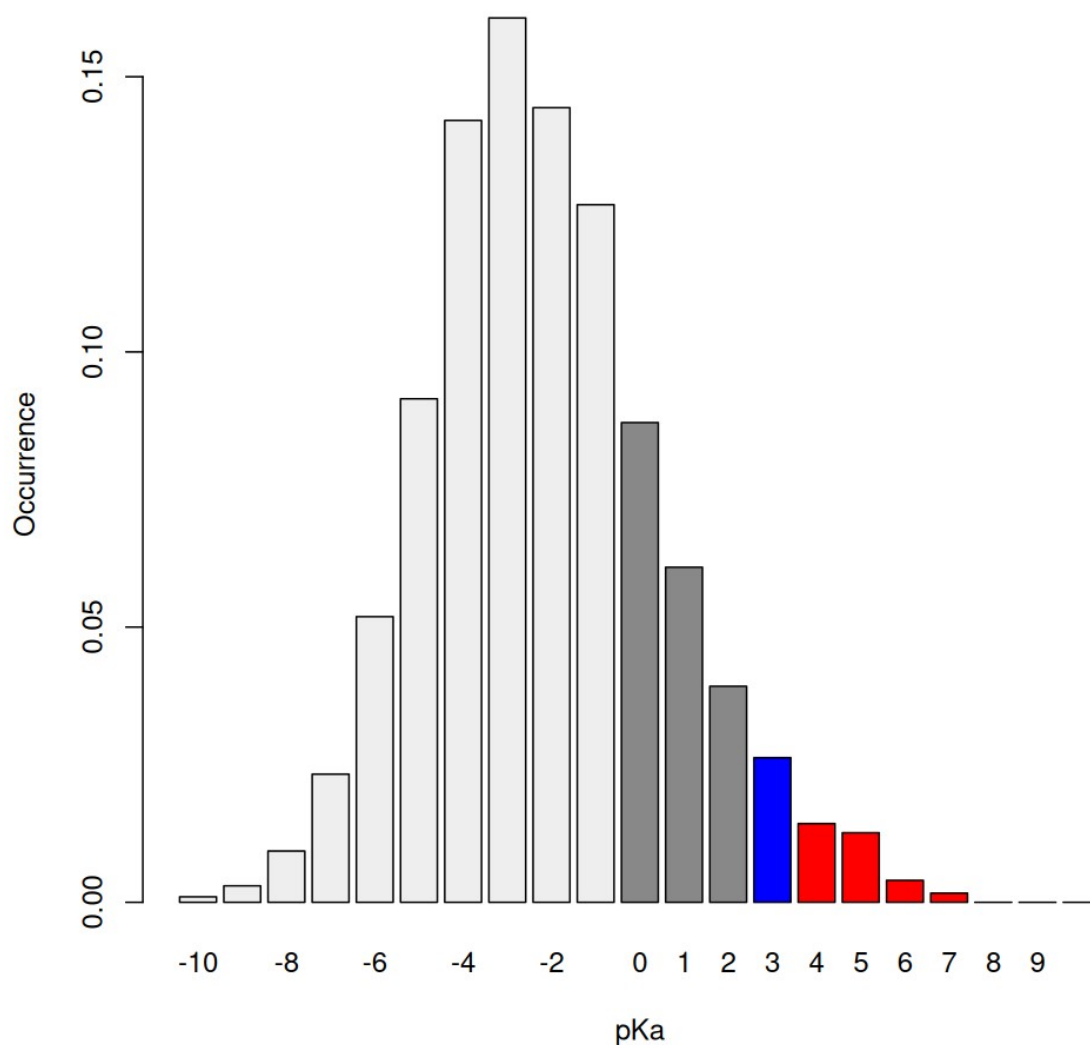


Figure S1

Relative occurrence of instantaneous pKa values of carbonate ions on the calcite nanoparticle surface. The colors correspond to the ones in Figure 5.