

Dehydrogenation vs. deprotonation of disaccharide molecules in vacuum, a thorough theoretical investigation (Supplementary Information)

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In the present paper, the following unified notations ${}^yX_{z';m';k'}$ of different calculated energies are used. Here, X is the calculated energy, y is the molecule of interest involved in the calculations (sucrose s , or trehalose t). The superscript $(z; m; k)$ refers to the system, for which a calculation is done, and the subscript $(z'; m'; k')$ refers to the system, from which the to-be-calculated system is extracted. Here, z is the system, which is being computed, and z' is the system, from which the to-be-computed system has been constructed. It can be: n , nominal molecule, H_i , dehydrogenated molecule with hydrogen atom H_i removed, or P_i , deprotonated molecule with proton i removed. The indices m and m' indicate the environment in which the system of interest is located: in the present study $m = m' = v$, that means vacuum. The indices k and k' indicate the kind of calculations: r , relaxed, or nr , not relaxed.

Similar notations are used for three characteristic energies corresponding to the changes of energies between different states of the molecules studied.

${}^yE_{br}^{Hi;v}$ is the break-up energy (no relaxation) of the nominal sucrose/trehalose(y) molecule into the dehydrogenated sucrose/trehalose + H-atom in vacuum, where ${}^yE_{n;v;r}^{Hi;v;nr}$ is the total energy of the non-relaxed dehydrogenated molecule, ${}^hE^v$ is the energy of the hydrogen atom and ${}^yE_{n;v;r}^{n;v;r}$ is the total energy of the relaxed nominal molecule:

$${}^yE_{br}^{Hi;v} = {}^yE_{n;v;r}^{Hi;v;nr} + {}^hE^v - {}^yE_{n;v;r}^{n;v;r}$$

${}^yE_{rel}^{Hi;v}$ is the relaxation energy of the relaxed dehydrogenated sucrose/trehalose(y) compared to the just broken-up dehydrogenated sucrose/trehalose in vacuum, where ${}^yE_{n;v;r}^{Hi;v;r}$ is the total energy of the relaxed dehydrogenated molecule:

$${}^yE_{rel}^{Hi;v} = {}^yE_{n;v;r}^{Hi;v;r} - {}^yE_{n;v;r}^{Hi;v;nr}$$

${}^yE_{rel}^{Pi;v}$ is the relaxation energy of the relaxed deprotonated sucrose/trehalose(y) compared to the just broken-up deprotonated sucrose/trehalose in vacuum, where ${}^yE_{n;v;r}^{Pi;v;r}$ and ${}^yE_{n;v;r}^{Pi;v;nr}$ are the total energy of the relaxed and non-relaxed deprotonated molecule, respectively:

$${}^yE_{rel}^{Pi;v} = {}^yE_{n;v;r}^{Pi;v;r} - {}^yE_{n;v;r}^{Pi;v;nr}$$

${}^yE_{bind}^{Hi;v}$ is the binding energy of the hydrogen atom:

$${}^yE_{bind}^{Hi;v} = {}^yE_{n;v;r}^{Hi;v;r} + {}^hE^v - {}^yE_{n;v;r}^{n;v;r}$$

Note that we also can write ${}^yE_{bind}^{Hi;v}$ as the sum of the break-up energy ${}^yE_{br}^{Hi;v}$ and the relaxation energy ${}^yE_{rel}^{Hi;v}$ of the dehydrogenated molecule: ${}^yE_{bind}^{Hi;v} = {}^yE_{br}^{Hi;v} + {}^yE_{rel}^{Hi;v}$.

I. Tables

I.1 Tables with characteristic energies of dehydrogenated and deprotonated conformations of sucrose, s1, s2, s3, and trehalose, t1, t2, t3, molecules

The labels of atoms in the columns 'Notation' of the Tables 3.1-1-3.1-12 correspond to the labels in Fig. 1 of the main paper. The order of hydrogen atoms in columns 'Notation' relates to their bonding with oxygen and carbon atoms in the molecules. Thus, s1H₁^{O(C)} means that we are dealing with the hydrogen atom no. 1 of the nominal sucrose conformation s1, where the hydrogen atom is bonded to an oxygen atom, which has a bond to a carbon atom. If we are describing a dehydrogenated molecule, then we add a "v" (for vacancy) between the name of the conformation and the hydrogen atom that has been removed, e.g., s1vH₁^{O(C)} refers to the sucrose conformation s1, where the hydrogen atom no. 1 has been removed. For the deprotonated molecule, we use P instead of H, to indicate that a proton and not a hydrogen atom has been removed, e.g., s1vP₁^{O(C)} refers to the sucrose conformation s1, where the proton no. 1 has been removed. If it is obvious which conformation is presented, the conformation label can be dropped.

NOTE 1: In Tables 3.1-1-3.1-12 and 3.2-1-3.2-9, different hydrogen atoms, in sucrose and trehalose molecules, are indicated by different colours depending on the type of oxygen and carbon atoms they are connected to: H_i^{O(C)} - black, H_i^{C(CCO)} - dark red, H_i^{C(COH)} - green, H_i^{C(COO)} - blue. In these tables, the bold font is used to indicate the cases of the breaking up of the molecules induced by their deprotonation.

NOTE 2: In the Tables 3.1-1-3.1-12, the sign of the energies ${}^y E_{br}^{Hi,v}$ and ${}^y E_{rel}^{Hi,v}$ are positive and negative, respectively, according to the definition of the break-up and relaxation energies.

NOTE 3: The total energy of a H-atom in vacuum is equal to ${}^h E^v = -0.12$ eV.

SI-Table 3.1-1. Characteristic energies of the sucrose s1, in eV. ${}^{s1} E_{n;v;nr}^{Hi,v}$: energy for nonoptimized dehydrogenated sucrose s1 and one separated hydrogen atom; ${}^{s1} E_{n;v;r}^{Hi,v}$: energy for optimized dehydrogenated sucrose s1 and one separated hydrogen atom; ${}^{s1} E_{br}^{Hi,v}$: break-up energy (no relaxation) of the nominal sucrose s1 into the dehydrogenated sucrose s1 + H-atom in vacuum; ${}^{s1} E_{rel}^{Hi,v}$: relaxation energy of the dehydrogenated sucrose s1 compared to the just broken-up dehydrogenated sucrose s1 in vacuum; ${}^{s1} E_{bind}^{Hi,v}$: binding energy of the hydrogen atom is the sum of the break-up energy ${}^{s1} E_{br}^{Hi,v}$ and the relaxation energy ${}^{s1} E_{rel}^{Hi,v}$ of the dehydrogenated molecule. The energy of the optimized sucrose s1 ${}^{s1} E^{n;v;r} = -227.059$ eV was used for calculation of energy differences in columns no. 4 and no. 6.

Notation	${}^{s1} E_{n;v;nr}^{Hi,v}$	${}^{s1} E_{n;v;r}^{Hi,v}$	${}^{s1} E_{br}^{Hi,v}$	${}^{s1} E_{rel}^{Hi,v}$	${}^{s1} E_{bind}^{Hi,v}$
s1vH ₁ ^{O(C)}	-221.130	-221.453	5.929	-0.323	5.606
s1vH ₂ ^{O(C)}	-221.290	-221.488	5.769	-0.198	5.571
s1vH ₃ ^{O(C)}	-221.072	-221.414	5.987	-0.342	5.645
s1vH ₄ ^{O(C)}	-221.274	-221.626	5.785	-0.352	5.433
s1vH ₅ ^{O(C)}	-221.108	-221.346	5.951	-0.238	5.713
s1vH ₆ ^{O(C)}	-221.185	-221.575	5.874	-0.390	5.484
s1vH ₇ ^{O(C)}	-220.942	-221.082	6.117	-0.140	5.977
s1vH ₈ ^{O(C)}	-221.073	-221.243	5.986	-0.170	5.816
s1vH ₉ ^{C(CCO)}	-221.447	-222.122	5.612	-0.675	4.937
s1vH ₁₀ ^{C(CCO)}	-221.547	-222.120	5.512	-0.573	4.939
s1vH ₁₁ ^{C(CCO)}	-221.412	-222.030	5.647	-0.618	5.029
s1vH ₁₂ ^{C(CCO)}	-221.657	-222.214	5.402	-0.557	4.845
s1vH ₁₃ ^{C(CCO)}	-221.342	-222.013	5.717	-0.671	5.046
s1vH ₁₄ ^{C(CCO)}	-221.239	-221.973	5.820	-0.734	5.086
s1vH ₁₅ ^{C(CCO)}	-221.61	-222.125	5.449	-0.515	4.934
s1vH ₁₆ ^{C(COH)}	-221.133	-222.154	5.926	-1.021	4.905
s1vH ₁₇ ^{C(COH)}	-221.097	-222.231	5.962	-1.134	4.828
s1vH ₁₈ ^{C(COH)}	-221.488	-222.203	5.571	-0.715	4.856
s1vH ₁₉ ^{C(COH)}	-220.908	-222.016	6.151	-1.108	5.043

$s1vH_{20}^{C(COH)}$	-221.352	-222.005	5.707	-0.653	5.054
$s1vH_{21}^{C(COH)}$	-221.583	-222.171	5.476	-0.588	4.888
$s1vH_{22}^{C(COO)}$	-221.413	-221.881	5.646	-0.468	5.178

SI-Table 3.1-2. Characteristic energies of the sucrose s2, in eV. $s^2E_{n,v;r}^{Hi;v;nr}$: energy for nonoptimized dehydrogenated sucrose s2 and one separated hydrogen atom; $s^2E_{n,v;r}^{Hi;v;r}$: energy for optimized dehydrogenated sucrose s2 and one separated hydrogen atom; $s^2E_{br}^{Hi;v}$: break-up energy (no relaxation) of the nominal sucrose s2 into the dehydrogenated sucrose s2 + H-atom in vacuum; $s^2E_{rel}^{Hi;v}$: relaxation energy of the dehydrogenated sucrose s2 compared to the just broken-up dehydrogenated sucrose s2 in vacuum; $s^2E_{bind}^{Hi;v}$: binding energy of the hydrogen atom is the sum of the break-up energy $s^2E_{br}^{Hi;v}$ and the relaxation energy $s^2E_{rel}^{Hi;v}$ of the dehydrogenated molecule. The energy of the optimized sucrose s2 $s^2E_{n,v;r}^{Hi;v;r} = -226.815$ eV was used for the calculation of energy differences in columns no. 4 and no. 6.

Notation	$s^2E_{n,v;r}^{Hi;v;nr}$	$s^2E_{n,v;r}^{Hi;v;r}$	$s^2E_{br}^{Hi;v}$	$s^2E_{rel}^{Hi;v}$	$s^2E_{bind}^{Hi;v}$
$s2vH_1^{0(C)}$	-221.137	-221.150	5.678	-0.013	5.665
$s2vH_2^{0(C)}$	-221.095	-221.289	5.720	-0.194	5.526
$s2vH_3^{0(C)}$	-220.992	-221.256	5.823	-0.264	5.559
$s2vH_4^{0(C)}$	-220.916	-221.231	5.899	-0.315	5.584
$s2vH_5^{0(C)}$	-220.875	-221.039	5.940	-0.164	5.776
$s2vH_6^{0(C)}$	-221.016	-221.345	5.799	-0.329	5.470
$s2vH_7^{0(C)}$	-220.832	-221.040	5.983	-0.208	5.775
$s2vH_8^{0(C)}$	-220.627	-220.745	6.188	-0.118	6.070
$s2vH_9^{C(CCO)}$	-221.273	-221.977	5.542	-0.704	4.838
$s2vH_{10}^{C(CCO)}$	-221.340	-221.811	5.475	-0.471	5.004
$s2vH_{11}^{C(CCO)}$	-221.196	-221.820	5.619	-0.624	4.995
$s2vH_{12}^{C(CCO)}$	-220.903	-221.600	5.912	-0.697	5.215
$s2vH_{13}^{C(CCO)}$	-221.135	-221.580	5.680	-0.445	5.235
$s2vH_{14}^{C(CCO)}$	-221.227	-221.823	5.588	-0.596	4.992
$s2vH_{15}^{C(CCO)}$	-221.301	-221.812	5.514	-0.511	5.003
$s2vH_{16}^{C(COH)}$	-221.344	-221.919	5.471	-0.575	4.896
$s2vH_{17}^{C(COH)}$	-220.693	-221.875	6.122	-1.182	4.940
$s2vH_{18}^{C(COH)}$	-221.058	-221.906	5.757	-0.848	4.909
$s2vH_{19}^{C(COH)}$	-220.859	-221.875	5.956	-1.016	4.94
$s2vH_{20}^{C(COH)}$	-221.348	-221.868	5.467	-0.520	4.947
$s2vH_{21}^{C(COH)}$	-221.183	-221.638	5.632	-0.455	5.177
$s2vH_{22}^{C(COO)}$	-221.137	-221.464	5.678	-0.327	5.351

SI-Table 3.1-3. Characteristic energies of the sucrose s3, in eV. $s^3E_{n,v;r}^{Hi;v;nr}$: energy for nonoptimized dehydrogenated sucrose s3 and one separated hydrogen atom; $s^3E_{n,v;r}^{Hi;v;r}$: energy for optimized dehydrogenated sucrose s3 and one separated hydrogen atom; $s^3E_{br}^{Hi;v}$: break-up energy (no relaxation) of the nominal sucrose s3 into the dehydrogenated sucrose s3 + H-atom in vacuum; $s^3E_{rel}^{Hi;v}$: relaxation energy of the dehydrogenated sucrose s3 compared to the just broken-up dehydrogenated sucrose s3 in vacuum; $s^3E_{bind}^{Hi;v}$: binding energy of the hydrogen atom is the sum of the break-up energy $s^3E_{br}^{Hi;v}$ and the relaxation energy $s^3E_{rel}^{Hi;v}$ of the dehydrogenated molecule. The energy of the optimized sucrose s3 $s^3E_{n,v;r}^{Hi;v;r} = -226.853$ eV was used for the calculation of energy differences in columns no. 4 and no. 6.

Notation	$s^3E_{n,v;r}^{Hi;v;nr}$	$s^3E_{n,v;r}^{Hi;v;r}$	$s^3E_{br}^{Hi;v}$	$s^3E_{rel}^{Hi;v}$	$s^3E_{bind}^{Hi;v}$
$s3vH_1^{0(C)}$	-220.975	-221.212	5.878	-0.237	5.641

$s3vH_2^{0(C)}$	-221.089	-221.352	5.764	-0.263	5.501
$s3vH_3^{0(C)}$	-220.809	-221.097	6.044	-0.288	5.756
$s3vH_4^{0(C)}$	-220.971	-221.246	5.882	-0.275	5.607
$s3vH_5^{0(C)}$	-220.901	-221.097	5.952	-0.196	5.756
$s3vH_6^{0(C)}$	-220.957	-221.241	5.896	-0.284	5.612
$s3vH_7^{0(C)}$	-220.904	-221.050	5.949	-0.146	5.803
$s3vH_8^{0(C)}$	-220.882	-221.038	5.971	-0.156	5.815
$s3vH_9^{C(CCO)}$	-221.346	-221.879	5.507	-0.533	4.974
$s3vH_{10}^{C(CCO)}$	-221.343	-221.897	5.510	-0.554	4.956
$s3vH_{11}^{C(CCO)}$	-221.206	-221.678	5.647	-0.472	5.175
$s3vH_{12}^{C(CCO)}$	-221.001	-221.862	5.852	-0.861	4.991
$s3vH_{13}^{C(CCO)}$	-221.194	-221.676	5.659	-0.482	5.177
$s3vH_{14}^{C(CCO)}$	-221.064	-221.847	5.789	-0.783	5.006
$s3vH_{15}^{C(CCO)}$	-221.386	-221.896	5.467	-0.510	4.957
$s3vH_{16}^{C(COH)}$	-221.300	-221.831	5.553	-0.531	5.022
$s3vH_{17}^{C(COH)}$	-220.750	-221.760	6.103	-1.010	5.093
$s3vH_{18}^{C(COH)}$	-220.793	-221.757	6.06	-0.964	5.096
$s3vH_{19}^{C(COH)}$	-220.744	-221.553	6.109	-0.809	5.300
$s3vH_{20}^{C(COH)}$	-221.095	-221.609	5.758	-0.514	5.244
$s3vH_{21}^{C(COH)}$	-221.246	-221.796	5.607	-0.550	5.057
$s3vH_{22}^{C(COO)}$	-221.171	-221.491	5.682	-0.320	5.362

SI-Table 3.1-4. Characteristic energies of the deprotonated sucrose s1, in eV. $s^1E_{n,v,r}^{Pi;v,nr}$: energy for nonoptimized deprotonated sucrose s1; $s^1E_{n,v,r}^{Pi;v,r}$: energy for optimized deprotonated sucrose s1; $s^1E_{br}^{Pi;v}$: break-up energy (no relaxation) of the nominal sucrose s1 molecule into the deprotonated one + proton in vacuum; $s^1E_{rel}^{Pi;v}$: relaxation energy of the deprotonated sucrose s1 compared to the just broken-up deprotonated one in vacuum; $s^1E_{bind}^{Pi;v}$: binding energy of the proton is the sum of the break-up energy $s^1E_{br}^{Pi;v}$ and the relaxation energy $s^1E_{rel}^{Pi;v}$ of the deprotonated molecule. The energy of the optimized sucrose s1 $s^1E_{n,v,r} = -227.10566$ eV was used for the calculation of energy differences in columns no. 4 and no. 6. Bold font is used for the cases of breaking the initial s1 molecule after deprotonation.

Notation	$s^1E_{n,v,r}^{Pi;v,nr}$	$s^1E_{n,v,r}^{Pi;v,r}$	$s^1E_{br}^{Pi;v}$	$s^1E_{rel}^{Pi;v}$	$s^1E_{bind}^{Pi;v}$
$s1vP_1^{0(C)}$	-223.913	-224.317	3.193	-0.404	2.788
$s1vP_2^{0(C)}$	-224.050	-224.366	3.056	-0.316	2.740
$s1vP_3^{0(C)}$	-223.994	-224.652	3.112	-0.658	2.453
$s1vP_4^{0(C)}$	-224.575	-225.365	2.531	-0.791	1.740
$s1vP_5^{0(C)}$	-223.786	-224.048	3.320	-0.262	3.057
$s1vP_6^{0(C)}$	-224.084	-224.576	3.022	-0.492	2.530
$s1vP_7^{0(C)}$	-223.350	-224.513	3.755	-1.162	2.593
$s1vP_8^{0(C)}$	-223.961	-224.489	3.145	-0.528	2.617
$s1vP_9^{C(CCO)}$	-223.120	-223.480	3.985	-0.359	3.626
$s1vP_{10}^{C(CCO)}$	-222.979	-223.284	4.127	-0.305	3.822
$s1vP_{11}^{C(CCO)}$	-223.179	-223.450	3.926	-0.270	3.656
$s1vP_{12}^{C(CCO)}$	-223.057	-224.804	4.049	-1.747	2.302
$s1vP_{13}^{C(CCO)}$	-222.939	-223.119	4.166	-0.180	3.986
$s1vP_{14}^{C(CCO)}$	-223.321	-225.315	3.784	-1.994	1.790

$s1vP_{15}^{C(CCO)}$	-222.952	-223.082	4.154	-0.130	4.023
$s1vP_{16}^{C(COH)}$	-222.932	-225.448	4.174	-2.517	1.657
$s1vP_{17}^{C(COH)}$	-222.587	-224.868	4.519	-2.281	2.238
$s1vP_{18}^{C(COH)}$	-222.954	-225.461	4.152	-2.508	1.644
$s1vP_{19}^{C(COH)}$	-223.035	-223.443	4.070	-0.408	3.662
$s1vP_{20}^{C(COH)}$	-223.100	-225.127	4.006	-2.028	1.978
$s1vP_{21}^{C(COH)}$	-222.768	-224.813	4.338	-2.046	2.292
$s1vP_{22}^{C(COO)}$	-223.260	-225.440	3.845	-2.180	1.665

SI-Table 3.1-5. Characteristic energies of the deprotonated sucrose s2, in eV. $s^2E_{n,v;r}^{Pi;v,nr}$: energy for nonoptimized deprotonated sucrose s2; $s^2E_{n,v;r}^{Pi;v,r}$: energy for optimized deprotonated sucrose s2; $s^2E_{br}^{Pi;v}$: break-up energy (no relaxation) of the nominal sucrose s2 molecule into the deprotonated one + proton in vacuum; $s^2E_{rel}^{Pi;v}$: relaxation energy of the deprotonated sucrose s2 compared to the just broken-up deprotonated one in vacuum; $s^2E_{bind}^{Pi;v}$: binding energy of the proton is the sum of the break-up energy $s^2E_{br}^{Pi;v}$ and the relaxation energy $s^2E_{rel}^{Pi;v}$ of the deprotonated molecule. The energy of the optimized sucrose s2 $s^2E_{n,v;r} = -226.86088$ eV was used for the calculation of energy differences in columns no. 4 and no. 6. Bold font is used for the cases of breaking the initial s2 molecule after deprotonation.

Notation	$s^2E_{n,v;r}^{Pi;v,nr}$	$s^2E_{n,v;r}^{Pi;v,r}$	$s^2E_{br}^{Pi;v}$	$s^2E_{rel}^{Pi;v}$	$s^2E_{bind}^{Pi;v}$
$s2vP_1^{O(C)}$	-223.917	-224.611	2.944	-0.694	2.250
$s2vP_2^{O(C)}$	-223.906	-224.296	2.955	-0.390	2.565
$s2vP_3^{O(C)}$	-224.094	-224.526	2.767	-0.432	2.335
$s2vP_4^{O(C)}$	-223.808	-224.209	3.052	-0.401	2.651
$s2vP_5^{O(C)}$	-223.787	-224.014	3.073	-0.227	2.847
$s2vP_6^{O(C)}$	-224.071	-224.374	2.790	-0.303	2.487
$s2vP_7^{O(C)}$	-223.796	-224.312	3.064	-0.516	2.548
$s2vP_8^{O(C)}$	-223.092	-224.332	3.769	-1.240	2.529
$s2vP_9^{C(CCO)}$	-223.029	-223.516	3.832	-0.487	3.344
$s2vP_{10}^{C(CCO)}$	-223.048	-223.379	3.813	-0.331	3.482
$s2vP_{11}^{C(CCO)}$	-222.774	-222.972	4.087	-0.198	3.889
$s2vP_{12}^{C(CCO)}$	-223.001	-224.926	3.859	-1.924	1.935
$s2vP_{13}^{C(CCO)}$	-222.857	-223.026	4.004	-0.169	3.835
$s2vP_{14}^{C(CCO)}$	-223.138	-223.566	3.723	-0.428	3.294
$s2vP_{15}^{C(CCO)}$	-222.896	-223.028	3.965	-0.132	3.833
$s2vP_{16}^{C(COH)}$	-222.646	-225.204	4.215	-2.557	1.657
$s2vP_{17}^{C(COH)}$	-222.560	-224.650	4.301	-2.090	2.211
$s2vP_{18}^{C(COH)}$	-222.521	-225.190	4.340	-2.669	1.671
$s2vP_{19}^{C(COH)}$	-222.909	-224.992	3.951	-2.083	1.869
$s2vP_{20}^{C(COH)}$	-222.901	-225.034	3.960	-2.134	1.826
$s2vP_{21}^{C(COH)}$	-222.574	-222.739	4.286	-0.165	4.122
$s2vP_{22}^{C(COO)}$	-222.939	-223.231	3.922	-0.292	3.630

SI-Table 3.1-6. Characteristic energies of the deprotonated sucrose s3, in eV. $s^3E_{n,v;r}^{Pi;v,nr}$: energy for nonoptimized deprotonated sucrose s3; $s^3E_{n,v;r}^{Pi;v,r}$: energy for optimized deprotonated sucrose s3; $s^3E_{br}^{Pi;v}$: break-up energy (no relaxation) of the nominal sucrose s3 molecule into the deprotonated one + proton in vacuum; $s^3E_{rel}^{Pi;v}$: relaxation energy of the deprotonated sucrose s3 compared to the just broken-up deprotonated one in vacuum; $s^3E_{bind}^{Pi;v}$: binding energy of the

proton is the sum of the break-up energy ${}^{s3}E_{br}^{Pi,v}$ and the relaxation energy ${}^{s3}E_{rel}^{Pi,v}$ of the deprotonated molecule. The energy of the optimized sucrose s3 ${}^{s3}E^{n,v;r} = -226.89725$ eV was used for the calculation of energy differences in columns no. 4 and no. 6. Bold font is used for the cases of breaking the initial s3 molecule after deprotonation.

Notation	${}^{s3}E_{n,v;r}^{Pi,v;nr}$	${}^{s3}E_{n,v;r}^{Pi,v;r}$	${}^{s3}E_{br}^{Pi,v}$	${}^{s3}E_{rel}^{Pi,v}$	${}^{s3}E_{bind}^{Pi,v}$
s3vP ₁ ^{0(C)}	-223.7663	-224.209	3.131	-0.443	2.688
s3vP ₂ ^{0(C)}	-224.011	-224.306	2.886	-0.295	2.591
s3vP ₃ ^{0(C)}	-223.710	-224.903	3.187	-1.194	1.994
s3vP ₄ ^{0(C)}	-224.083	-224.930	2.814	-0.847	1.968
s3vP ₅ ^{0(C)}	-223.654	-223.911	3.243	-0.257	2.986
s3vP ₆ ^{0(C)}	-223.991	-225.018	2.906	-1.027	1.879
s3vP ₇ ^{0(C)}	-223.541	-224.981	3.356	-1.440	1.916
s3vP ₈ ^{0(C)}	-223.666	-223.956	3.231	-0.290	2.941
s3vP ₉ ^{C(CCO)}	-223.208	-223.462	3.689	-0.253	3.436
s3vP ₁₀ ^{C(CCO)}	-222.840	-223.172	4.057	-0.332	3.725
s3vP ₁₁ ^{C(CCO)}	-222.972	-223.179	3.925	-0.207	3.718
s3vP₁₂^{C(CCO)}	-222.825	-224.432	4.072	-1.606	2.465
s3vP ₁₃ ^{C(CCO)}	-222.778	-225.037	4.119	-2.259	1.860
s3vP₁₄^{C(CCO)}	-223.208	-225.307	3.689	-2.099	1.590
s3vP ₁₅ ^{C(CCO)}	-222.805	-222.952	4.092	-0.146	3.946
s3vP₁₆^{C(COH)}	-222.828	-225.120	4.069	-2.291	1.778
s3vP₁₇^{C(COH)}	-222.433	-224.766	4.464	-2.333	2.132
s3vP₁₈^{C(COH)}	-222.728	-225.122	4.169	-2.394	1.775
s3vP₁₉^{C(COH)}	-222.838	-225.288	4.059	-2.450	1.609
s3vP₂₀^{C(COH)}	-222.957	-224.890	3.940	-1.933	2.007
s3vP₂₁^{C(COH)}	-222.553	-224.755	4.344	-2.202	2.142
s3vP ₂₂ ^{C(COO)}	-223.040	-223.418	3.857	-0.377	3.479

SI-Table 3.1-7. Characteristic energies of the trehalose t1, in eV. ${}^{t1}E_{n,v;r}^{Hi,v;nr}$: energy for nonoptimized dehydrogenated trehalose t1 and one separated hydrogen atom; ${}^{t1}E_{n,v;r}^{Hi,v;r}$: energy for optimized dehydrogenated trehalose t1 and one separated hydrogen atom; ${}^{t1}E_{br}^{Hi,v}$: break-up energy (no relaxation) of the nominal trehalose t1 into the dehydrogenated trehalose t1 + H-atom in vacuum; ${}^{t1}E_{rel}^{Hi,v}$: relaxation energy of the dehydrogenated trehalose t1 compared to the just broken-up dehydrogenated trehalose t1 in vacuum; ${}^{t1}E_{bind}^{Hi,v}$: binding energy of the hydrogen atom is the sum of the break-up energy ${}^{t1}E_{br}^{Hi,v}$ and the relaxation energy ${}^{t1}E_{rel}^{Hi,v}$ of the dehydrogenated molecule. The energy of the optimized trehalose t1 ${}^{t1}E^{n,v;r} = -226.962$ eV was used for the calculation of energy differences in columns no. 4 and no. 6.

Notation	${}^{t1}E_{n,v;r}^{Hi,v;nr}$	${}^{t1}E_{n,v;r}^{Hi,v;r}$	${}^{t1}E_{br}^{Hi,v}$	${}^{t1}E_{rel}^{Hi,v}$	${}^{t1}E_{bind}^{Hi,v}$
t1vH ₁ ^{0(C)}	-220.843	-221.002	6.119	-0.159	5.960
t1vH ₂ ^{0(C)}	-221.021	-221.232	5.941	-0.211	5.730
t1vH ₃ ^{0(C)}	-221.035	-221.234	5.927	-0.199	5.728
t1vH ₄ ^{0(C)}	-220.863	-221.064	6.099	-0.201	5.898
t1vH ₅ ^{0(C)}	-220.867	-221.068	6.095	-0.201	5.894
t1vH ₆ ^{0(C)}	-220.840	-220.990	6.122	-0.150	5.972
t1vH ₇ ^{0(C)}	-220.842	-221.063	6.120	-0.221	5.899
t1vH ₈ ^{0(C)}	-220.843	-221.063	6.119	-0.220	5.899
t1vH ₉ ^{C(CCO)}	-221.279	-221.850	5.683	-0.571	5.112

$t1vH_{10}^{C(CCO)}$	-221.156	-221.792	5.806	-0.636	5.770
$t1vH_{11}^{C(CCO)}$	-221.237	-221.732	5.725	-0.495	5.230
$t1vH_{12}^{C(CCO)}$	-221.283	-221.864	5.679	-0.581	5.098
$t1vH_{13}^{C(CCO)}$	-221.243	-221.740	5.719	-0.497	5.222
$t1vH_{14}^{C(CCO)}$	-221.390	-221.910	5.572	-0.520	5.052
$t1vH_{15}^{C(CCO)}$	-221.391	-221.925	5.571	-0.534	5.037
$t1vH_{16}^{C(CCO)}$	-221.156	-221.644	5.806	-0.488	5.318
$t1vH_{17}^{C(COH)}$	-221.257	-221.821	5.705	-0.564	5.141
$t1vH_{18}^{C(COH)}$	-220.759	-221.840	6.203	-1.081	5.122
$t1vH_{19}^{C(COH)}$	-220.747	-221.834	6.215	-1.087	5.128
$t1vH_{20}^{C(COH)}$	-221.282	-221.838	5.68	-0.556	5.124
$t1vH_{21}^{C(COO)}$	-221.232	-221.579	5.730	-0.347	5.383
$t1vH_{22}^{C(COO)}$	-221.224	-221.578	5.738	-0.354	5.384

SI-Table 3.1-8. Characteristic energies of the trehalose t2, in eV. $t^2E_{n,v;r}^{Hi;v,nr}$: energy for nonoptimized dehydrogenated trehalose t2 and one separated hydrogen atom; $t^2E_{n,v;r}^{Hi;v,r}$: energy for optimized dehydrogenated trehalose t2 and one separated hydrogen atom; $t^2E_{br}^{Hi;v}$: break-up energy (no relaxation) of the nominal trehalose t2 into the dehydrogenated trehalose t2 + H-atom in vacuum; $t^2E_{rel}^{Hi;v}$: relaxation energy of the dehydrogenated trehalose t2 compared to the just broken-up dehydrogenated trehalose t2 in vacuum; $t^2E_{bind}^{Hi;v}$: binding energy of the hydrogen atom is the sum of the break-up energy $t^2E_{br}^{Hi;v}$ and the relaxation energy $t^2E_{rel}^{Hi;v}$ of the dehydrogenated molecule. The energy of the optimized trehalose t2 $t^2E^{n,v;r} = -226.831$ eV was used for the calculation of energy differences in columns no. 4 and no. 6.

Notation	$t^2E_{n,v;r}^{Hi;v,nr}$	$t^2E_{n,v;r}^{Hi;v,r}$	$t^2E_{br}^{Hi;v}$	$t^2E_{rel}^{Hi;v}$	$t^2E_{bind}^{Hi;v}$
$t2vH_1^{O(C)}$	-220.833	-220.987	5.998	-0.154	5.844
$t2vH_2^{O(C)}$	-221.069	-221.254	5.762	-0.185	5.577
$t2vH_3^{O(C)}$	-220.903	-221.393	5.928	-0.490	5.438
$t2vH_4^{O(C)}$	-220.871	-221.294	5.960	-0.423	5.537
$t2vH_5^{O(C)}$	-220.981	-221.261	5.850	-0.280	5.570
$t2vH_6^{O(C)}$	-220.913	-221.061	5.918	-0.148	5.770
$t2vH_7^{O(C)}$	-220.892	-221.100	5.939	-0.208	5.731
$t2vH_8^{O(C)}$	-220.874	-221.058	5.957	-0.184	5.773
$t2vH_9^{C(CCO)}$	-221.335	-221.892	5.496	-0.557	4.939
$t2vH_{10}^{C(CCO)}$	-221.142	-221.631	5.689	-0.489	5.200
$t2vH_{11}^{C(CCO)}$	-221.277	-221.862	5.554	-0.585	4.969
$t2vH_{12}^{C(CCO)}$	-221.232	-221.772	5.599	-0.540	5.059
$t2vH_{13}^{C(CCO)}$	-221.163	-221.683	5.668	-0.520	5.148
$t2vH_{14}^{C(CCO)}$	-221.373	-221.906	5.458	-0.533	4.925
$t2vH_{15}^{C(CCO)}$	-221.344	-221.850	5.487	-0.506	4.981
$t2vH_{16}^{C(CCO)}$	-221.171	-221.623	5.660	-0.452	5.208
$t2vH_{17}^{C(COH)}$	-221.326	-221.848	5.505	-0.522	4.983
$t2vH_{18}^{C(COH)}$	-221.284	-221.979	5.547	-0.695	4.852
$t2vH_{19}^{C(COH)}$	-220.770	-221.809	6.061	-1.039	5.022
$t2vH_{20}^{C(COH)}$	-220.847	-221.983	5.984	-1.136	4.848
$t2vH_{21}^{C(COO)}$	-221.200	-221.532	5.631	-0.332	5.299

$t2vH_{22}^{C(COO)}$	-221.199	-221.514	5.632	-0.315	5.317
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SI-Table 3.1-9. Characteristic energies of the trehalose t3, in eV. $t^3E_{n,v;r}^{Hi;v,nr}$: energy for nonoptimized dehydrogenated trehalose t3 and one separated hydrogen atom; $t^3E_{n,v;r}^{Hi;v,r}$: energy for optimized dehydrogenated trehalose t3 and one separated hydrogen atom; $t^3E_{br}^{Hi;v}$: break-up energy (no relaxation) of the nominal trehalose t3 into the dehydrogenated trehalose t3 + H-atom in vacuum; $t^3E_{rel}^{Hi;v}$: relaxation energy of the dehydrogenated trehalose t3 compared to the just broken-up dehydrogenated trehalose t3 in vacuum; $t^3E_{bind}^{Hi;v}$: binding energy of the hydrogen atom is the sum of the break-up energy $t^3E_{br}^{Hi;v}$ and the relaxation energy $t^3E_{rel}^{Hi;v}$ of the dehydrogenated molecule. The energy of the optimized trehalose t3 $t^3E^{n;v;r} = -226.828$ eV was used for the calculation of energy differences in columns no. 4 and no. 6.

Notation	$t^3E_{n,v;r}^{Hi;v,nr}$	$t^3E_{n,v;r}^{Hi;v,r}$	$t^3E_{br}^{Hi;v}$	$t^3E_{rel}^{Hi;v}$	$t^3E_{bind}^{Hi;v}$
$t3vH_1^{O(C)}$	-220.795	-220.968	6.033	-0.173	5.86
$t3vH_2^{O(C)}$	-220.886	-221.122	5.942	-0.236	5.706
$t3vH_3^{O(C)}$	-221.003	-221.363	5.825	-0.360	5.465
$t3vH_4^{O(C)}$	-220.895	-221.089	5.933	-0.194	5.739
$t3vH_5^{O(C)}$	-220.986	-221.233	5.842	-0.247	5.595
$t3vH_6^{O(C)}$	-221.046	-221.241	5.782	-0.195	5.587
$t3vH_7^{O(C)}$	-220.900	-221.147	5.928	-0.247	5.681
$t3vH_8^{O(C)}$	-220.861	-221.409	5.967	-0.548	5.419
$t3vH_9^{C(CCO)}$	-221.367	-221.902	5.461	-0.535	4.926
$t3vH_{10}^{C(CCO)}$	-221.174	-221.680	5.654	-0.506	5.148
$t3vH_{11}^{C(CCO)}$	-220.925	-221.920	5.903	-0.995	4.908
$t3vH_{12}^{C(CCO)}$	-221.266	-221.835	5.562	-0.569	4.993
$t3vH_{13}^{C(CCO)}$	-221.409	-221.926	5.419	-0.517	4.902
$t3vH_{14}^{C(CCO)}$	-221.362	-221.919	5.466	-0.557	4.909
$t3vH_{15}^{C(CCO)}$	-221.388	-221.868	5.440	-0.480	4.960
$t3vH_{16}^{C(CCO)}$	-221.168	-221.633	5.660	-0.465	5.195
$t3vH_{17}^{C(COH)}$	-221.363	-221.878	5.465	-0.515	4.95
$t3vH_{18}^{C(COH)}$	-221.109	-221.630	5.719	-0.521	5.198
$t3vH_{19}^{C(COH)}$	-220.817	-221.904	6.011	-1.087	4.924
$t3vH_{20}^{C(COH)}$	-221.202	-221.653	5.626	-0.451	5.175
$t3vH_{21}^{C(COO)}$	-221.246	-221.656	5.582	-0.410	5.172
$t3vH_{22}^{C(COO)}$	-221.180	-221.543	5.648	-0.363	5.285

SI-Table 3.1-10. Characteristic energies of the deprotonated trehalose t1, in eV. $t^1E_{n,v;r}^{Pi;v,nr}$: energy for nonoptimized deprotonated trehalose t1; $t^1E_{n,v;r}^{Pi;v,r}$: energy for optimized deprotonated trehalose t1; $t^1E_{br}^{Pi;v}$: break-up energy (no relaxation) of the nominal trehalose t1 molecule into the deprotonated one + proton in vacuum; $t^1E_{rel}^{Pi;v}$: relaxation energy of the deprotonated trehalose t1 compared to the just broken-up deprotonated one in vacuum; $t^1E_{bind}^{Pi;v}$: binding energy of the proton is the sum of the break-up energy $t^1E_{br}^{Pi;v}$ and the relaxation energy $t^1E_{rel}^{Pi;v}$ of the deprotonated molecule. The energy of the optimized trehalose t1 $t^1E^{n;v;r} = -227.00395$ eV was used for the calculation of energy differences in columns no. 4 and no. 6. Bold font is used for the cases of breaking the initial t1 molecule after deprotonation.

Notation	$t^1E_{n,v;r}^{Pi;v,nr}$	$t^1E_{n,v;r}^{Pi;v,r}$	$t^1E_{br}^{Pi;v}$	$t^1E_{rel}^{Pi;v}$	$t^1E_{bind}^{Pi;v}$
$t1vP_1^{O(C)}$	-223.655	-225.230	3.349	-1.576	1.773
$t1vP_2^{O(C)}$	-224.155	-224.570	2.849	-0.415	2.434
$t1vP_3^{O(C)}$	-224.169	-224.575	2.835	-0.406	2.428
$t1vP_4^{O(C)}$	-223.877	-224.825	3.127	-0.949	2.178
$t1vP_5^{O(C)}$	-223.891	-224.800	3.112	-0.908	2.204

$t1vP_6^{O(C)}$	-223.617	-225.210	3.387	-1.593	1.794
$t1vP_7^{O(C)}$	-223.743	-224.035	3.261	-0.292	2.969
$t1vP_8^{O(C)}$	-223.741	-224.161	3.263	-0.421	2.843
$t1vP_9^{C(CCO)}$	-222.948	-223.402	4.056	-0.454	3.602
$t1vP_{10}^{C(CCO)}$	-222.777	-225.227	4.227	-2.450	1.777
$t1vP_{11}^{C(CCO)}$	-223.028	-223.370	3.976	-0.343	3.634
$t1vP_{12}^{C(CCO)}$	-222.935	-223.425	4.069	-0.490	3.579
$t1vP_{13}^{C(CCO)}$	-223.024	-223.359	3.980	-0.336	3.645
$t1vP_{14}^{C(CCO)}$	-222.877	-223.196	4.127	-0.319	3.807
$t1vP_{15}^{C(CCO)}$	-222.877	-223.211	4.127	-0.335	3.793
$t1vP_{16}^{C(CCO)}$	-222.771	-225.230	4.233	-2.459	1.774
$t1vP_{17}^{C(COH)}$	-222.635	-224.695	4.369	-2.060	2.309
$t1vP_{18}^{C(COH)}$	-222.521	-224.803	4.483	-2.282	2.201
$t1vP_{19}^{C(COH)}$	-222.533	-224.741	4.471	-2.208	2.263
$t1vP_{20}^{C(COH)}$	-222.624	-224.711	4.380	-2.088	2.293
$t1vP_{21}^{C(COO)}$	-223.072	-223.427	3.932	-0.355	3.577
$t1vP_{22}^{C(COO)}$	-223.070	-223.555	3.934	-0.485	3.448

SI-Table 3.1-11. Characteristic energies of the deprotonated trehalose t2, in eV. $t^2E_{n,v,r}^{Pi;v,nr}$: energy for nonoptimized deprotonated trehalose t2; $t^2E_{n,v,r}^{Pi;v,r}$: energy for optimized deprotonated trehalose t2; $t^2E_{br}^{Pi;m}$: break-up energy (no relaxation) of the nominal trehalose t2 molecule into the deprotonated one + proton in vacuum; $t^2E_{rel}^{Pi;v}$: relaxation energy of the deprotonated trehalose t2 compared to the just broken-up deprotonated one in vacuum; $t^2E_{bind}^{Pi;v}$: binding energy of the proton is the sum of the break-up energy $t^2E_{br}^{Pi;v}$ and the relaxation energy $t^2E_{rel}^{Pi;v}$ of the deprotonated molecule. The energy of the optimized trehalose t2 $t^2E^{n,v,r} = -226.88122$ eV was used for the calculation of energy differences in columns no. 4 and no. 6. Bold font is used for the cases of breaking the initial t2 molecule after deprotonation.

Notation	$t^2E_{n,v,r}^{Pi;v,nr}$	$t^2E_{n,v,r}^{Pi;v,r}$	$t^2E_{br}^{Pi;v}$	$t^2E_{rel}^{Pi;v}$	$t^2E_{bind}^{Pi;v}$
$t2vP_1^{O(C)}$	-223.327	-223.872	3.554	-0.545	3.009
$t2vP_2^{O(C)}$	-224.224	-224.626	2.658	-0.403	2.255
$t2vP_3^{O(C)}$	-224.027	-224.863	2.8544	-0.836	2.018
$t2vP_4^{O(C)}$	-223.937	-224.754	2.944	-0.816	2.128
$t2vP_5^{O(C)}$	-223.828	-224.222	3.0534	-0.394	2.660
$t2vP_6^{O(C)}$	-223.595	-224.858	3.286	-1.262	2.023
$t2vP_7^{O(C)}$	-223.616	-223.879	3.265	-0.262	3.002
$t2vP_8^{O(C)}$	-223.798	-224.058	3.083	-0.260	2.823
$t2vP_9^{C(CCO)}$	-222.842	-223.103	4.039	-0.261	3.778
$t2vP_{10}^{C(CCO)}$	-222.633	-223.257	4.248	-0.624	3.624
$t2vP_{11}^{C(CCO)}$	-222.909	-224.711	3.972	-1.802	2.170
$t2vP_{12}^{C(CCO)}$	-223.005	-223.272	3.877	-0.267	3.610
$t2vP_{13}^{C(CCO)}$	-223.104	-223.441	3.778	-0.338	3.440
$t2vP_{14}^{C(CCO)}$	-222.774	-222.924	4.107	-0.150	3.957
$t2vP_{15}^{C(CCO)}$	-222.925	-223.079	3.957	-0.155	3.802
$t2vP_{16}^{C(CCO)}$	-222.965	-223.282	3.917	-0.317	3.599
$t2vP_{17}^{C(COH)}$	-222.502	-224.706	4.379	-2.203	2.176

$t2vP_{18}^{C(COH)}$	-222.624	-225.204	4.257	-2.580	1.677
$t2vP_{19}^{C(COH)}$	-222.378	-224.691	4.503	-2.313	2.190
$t2vP_{20}^{C(COH)}$	-222.514	-225.229	4.367	-2.715	1.6521
$t2vP_{21}^{C(COO)}$	-223.133	-223.747	3.749	-0.614	3.134
$t2vP_{22}^{C(COO)}$	-223.216	-223.651	3.665	-0.435	3.230

SI-Table 3.1-12. Characteristic energies of the deprotonated trehalose t3, in eV. $t^3E_{n,v;r}^{Pi;v;nr}$: energy for nonoptimized deprotonated trehalose t3; $t^3E_{n,v;r}^{Pi;v;r}$: energy for optimized deprotonated trehalose t3; $t^3E_{br}^{Pi;m}$: break-up energy (no relaxation) of the nominal trehalose t3 molecule into the deprotonated one + proton in vacuum; $t^3E_{rel}^{Pi;v}$: relaxation energy of the deprotonated trehalose t3 compared to the just broken-up deprotonated one in vacuum; $t^3E_{bind}^{Pi;v}$: binding energy of the proton is the sum of the break-up energy $t^3E_{br}^{Pi;v}$ and the relaxation energy $t^3E_{rel}^{Pi;v}$ of the deprotonated molecule. The energy of the optimized trehalose t3 $t^3E^{n;v;r} = -226.86695$ eV was used for the calculation of energy differences in columns no. 4 and no. 6. Bold font is used for the cases of breaking the initial t3 molecule after deprotonation.

Notation	$t^3E_{n,v;r}^{Pi;v;nr}$	$t^3E_{n,v;r}^{Pi;v;r}$	$t^3E_{br}^{Pi;v}$	$t^3E_{rel}^{Pi;v}$	$t^3E_{bind}^{Pi;v}$
$t3vP_1^{0(C)}$	-223.178	-223.395	3.689	-0.216	3.472
$t3vP_2^{0(C)}$	-223.611	-223.863	3.255	-0.252	3.004
$t3vP_3^{0(C)}$	-223.910	-224.248	2.957	-0.338	2.619
$t3vP_4^{0(C)}$	-223.661	-224.002	3.206	-0.341	2.865
$t3vP_5^{0(C)}$	-223.733	-224.366	3.134	-0.633	2.501
$t3vP_6^{0(C)}$	-224.250	-224.888	2.617	-0.638	1.979
$t3vP_7^{0(C)}$	-223.543	-223.773	3.323	-0.230	3.094
$t3vP_8^{0(C)}$	-223.611	-225.005	3.256	-1.393	1.862
$t3vP_9^{C(CCO)}$	-222.845	-223.121	4.022	-0.276	3.746
$t3vP_{10}^{C(CCO)}$	-222.585	-222.709	4.281	-0.123	4.158
$t3vP_{11}^{C(CCO)}$	-222.804	-223.812	4.063	-1.008	3.055
$t3vP_{12}^{C(CCO)}$	-222.690	-222.983	4.177	-0.293	3.884
$t3vP_{13}^{C(CCO)}$	-222.784	-224.226	4.083	-1.442	2.641
$t3vP_{14}^{C(CCO)}$	-222.723	-222.846	4.143	-0.123	4.021
$t3vP_{15}^{C(CCO)}$	-222.783	-222.946	4.084	-0.163	3.921
$t3vP_{16}^{C(CCO)}$	-222.842	-223.106	4.025	-0.264	3.761
$t3vP_{17}^{C(COH)}$	-222.444	-222.598	4.423	-0.154	4.268
$t3vP_{18}^{C(COH)}$	-222.746	-222.905	4.120	-0.158	3.962
$t3vP_{19}^{C(COH)}$	-222.304	-224.410	4.563	-2.106	2.457
$t3vP_{20}^{C(COH)}$	-222.737	-222.894	4.130	-0.157	3.973
$t3vP_{21}^{C(COO)}$	-222.766	-222.924	4.101	-0.158	3.943
$t3vP_{22}^{C(COO)}$	-222.896	-224.308	3.971	-1.412	2.559

I.2 Tables presenting electronic properties of nominal, dehydrogenated and deprotonated conformations of sucrose and trehalose molecules

SI-Table 3.2-1. NACs (q), in q_e , DMs (P), in at. units, and BOs (B) for atoms of the nominal sucrose s1 and trehalose t1 molecules. For the specific definition of bond orders, c.f. [23]

sucrose s1				trehalose t1			
Atoms of s1	q	P	B	Atoms of t1	q	P	B
$H_1^{O(C)}$	0.367	0.041	0.932	$H_1^{O(C)}$	0.339	0.041	0.923
$H_2^{O(C)}$	0.358	0.043	1.003	$H_2^{O(C)}$	0.357	0.041	0.890
$H_3^{O(C)}$	0.348	0.026	0.879	$H_3^{O(C)}$	0.358	0.042	0.889
$H_4^{O(C)}$	0.357	0.042	0.983	$H_4^{O(C)}$	0.363	0.041	0.893
$H_5^{O(C)}$	0.362	0.041	0.949	$H_5^{O(C)}$	0.361	0.042	0.893
$H_6^{O(C)}$	0.351	0.039	0.975	$H_6^{O(C)}$	0.338	0.041	0.926
$H_7^{O(C)}$	0.338	0.029	0.897	$H_7^{O(C)}$	0.361	0.041	0.894
$H_8^{O(C)}$	0.313	0.018	0.969	$H_8^{O(C)}$	0.362	0.041	0.893
$H_9^{C(CCO)}$	0.056	0.055	0.939	$H_9^{C(CCO)}$	0.064	0.056	0.942
$H_{10}^{C(CCO)}$	0.050	0.054	0.979	$H_{10}^{C(CCO)}$	0.059	0.053	0.976
$H_{11}^{C(CCO)}$	0.071	0.052	0.936	$H_{11}^{C(CCO)}$	0.052	0.053	0.955
$H_{12}^{C(CCO)}$	0.050	0.051	0.945	$H_{12}^{C(CCO)}$	0.062	0.056	0.943
$H_{13}^{C(CCO)}$	0.059	0.052	0.950	$H_{13}^{C(CCO)}$	0.052	0.053	0.954
$H_{14}^{C(CCO)}$	0.077	0.048	0.965	$H_{14}^{C(CCO)}$	0.039	0.050	0.954
$H_{15}^{C(CCO)}$	0.045	0.050	1.003	$H_{15}^{C(CCO)}$	0.039	0.050	0.953
$H_{16}^{C(COH)}$	0.085	0.047	0.960	$H_{16}^{C(COH)}$	0.060	0.053	0.970
$H_{17}^{C(COH)}$	0.100	0.051	0.883	$H_{17}^{C(COH)}$	0.051	0.043	0.966
$H_{18}^{C(COH)}$	0.059	0.044	0.930	$H_{18}^{C(COH)}$	0.096	0.050	0.938
$H_{19}^{C(COH)}$	0.110	0.049	0.920	$H_{19}^{C(COH)}$	0.097	0.050	0.939
$H_{20}^{C(COH)}$	0.074	0.045	0.958	$H_{20}^{C(COH)}$	0.050	0.043	0.969
$H_{21}^{C(COH)}$	0.051	0.043	0.884	$H_{21}^{C(COO)}$	0.038	0.067	0.947
$H_{22}^{C(COO)}$	0.040	0.071	0.963	$H_{22}^{C(COO)}$	0.038	0.067	0.950
C	0.269	0.101	3.904	C	0.266	0.088	3.932
C	0.330	0.086	3.806	C	0.072	0.115	3.917
C	0.096	0.069	3.934	C	0.074	0.117	3.917
C	0.115	0.082	3.913	C	0.121	0.107	3.902
C	0.070	0.116	3.918	C	0.108	0.104	3.901
C	0.033	0.133	3.914	C	0.045	0.116	3.923
C	-0.040	0.135	3.924	C	0.123	0.106	3.906
C	0.061	0.122	3.939	C	0.085	0.067	3.852
C	0.109	0.109	3.917	C	0.266	0.088	3.931
C	0.044	0.125	3.899	C	0.113	0.105	3.898
C	0.124	0.108	3.811	C	0.045	0.116	3.921
C	0.116	0.108	3.928	C	0.086	0.067	3.850
O	-0.498	0.154	2.500	O	-0.508	0.138	2.163
O	-0.491	0.139	2.371	O	-0.498	0.165	2.163

O	-0.504	0.156	2.302	O	-0.497	0.164	2.166
O	-0.522	0.133	2.179	O	-0.336	0.174	2.434
O	-0.31	0.155	2.173	O	-0.3361	0.173	2.438
O	-0.508	0.135	2.236	O	-0.5091	0.138	2.162
O	-0.456	0.160	2.199	O	-0.5236	0.137	2.173
O	-0.523	0.139	2.459	O	-0.527	0.137	2.169
O	-0.347	0.167	2.168	O	-0.4987	0.138	2.203
O	-0.520	0.135	2.161	O	-0.4971	0.139	2.206
O	-0.365	0.134	2.206	O	-0.3127	0.130	2.513

SI-Table 3.2-2. NACs (q), in q_e , DMs (P), in at. units, and BOs (B) for atoms of the nominal sucrose s2 and trehalose t2 molecules.

sucrose s2				trehalose t2			
Atoms of s1	q	P	B	Atoms of t1	q	P	B
$H_1^{O(C)}$	0.360	0.041	0.895	$H_1^{O(C)}$	0.338	0.041	0.924
$H_2^{O(C)}$	0.353	0.043	0.895	$H_2^{O(C)}$	0.356	0.043	0.890
$H_3^{O(C)}$	0.342	0.040	0.923	$H_3^{O(C)}$	0.324	0.021	1.008
$H_4^{O(C)}$	0.344	0.038	0.915	$H_4^{O(C)}$	0.363	0.042	0.892
$H_5^{O(C)}$	0.364	0.042	0.888	$H_5^{O(C)}$	0.359	0.041	0.900
$H_6^{O(C)}$	0.335	0.033	0.970	$H_6^{O(C)}$	0.336	0.035	0.931
$H_7^{O(C)}$	0.347	0.036	0.917	$H_7^{O(C)}$	0.363	0.041	0.891
$H_8^{O(C)}$	0.325	0.021	1.018	$H_8^{O(C)}$	0.362	0.042	0.892
$H_9^{C(CCO)}$	0.049	0.051	0.967	$H_9^{C(CCO)}$	0.041	0.053	0.973
$H_{10}^{C(CCO)}$	0.039	0.052	0.966	$H_{10}^{C(CCO)}$	0.065	0.055	0.949
$H_{11}^{C(CCO)}$	0.072	0.051	0.935	$H_{11}^{C(CCO)}$	0.068	0.052	0.938
$H_{12}^{C(CCO)}$	0.084	0.054	0.925	$H_{12}^{C(CCO)}$	0.063	0.055	0.941
$H_{13}^{C(CCO)}$	0.050	0.051	0.984	$H_{13}^{C(CCO)}$	0.054	0.054	0.953
$H_{14}^{C(CCO)}$	0.065	0.049	0.955	$H_{14}^{C(CCO)}$	0.041	0.050	0.954
$H_{15}^{C(CCO)}$	0.045	0.051	0.947	$H_{15}^{C(CCO)}$	0.044	0.051	0.947
$H_{16}^{C(COH)}$	0.036	0.043	0.993	$H_{16}^{C(COH)}$	0.046	0.052	0.980
$H_{17}^{C(COH)}$	0.099	0.051	0.937	$H_{17}^{C(COH)}$	0.048	0.042	0.971
$H_{18}^{C(COH)}$	0.075	0.048	0.948	$H_{18}^{C(COH)}$	0.072	0.049	0.962
$H_{19}^{C(COH)}$	0.097	0.045	0.944	$H_{19}^{C(COH)}$	0.096	0.051	0.940
$H_{20}^{C(COH)}$	0.072	0.044	0.967	$H_{20}^{C(COH)}$	0.082	0.046	0.944
$H_{21}^{C(COH)}$	0.061	0.044	0.961	$H_{21}^{C(COO)}$	0.043	0.065	0.942
$H_{22}^{C(COO)}$	0.062	0.072	0.960	$H_{22}^{C(COO)}$	0.034	0.063	0.950
C	0.276	0.100	3.898	C	0.274	0.093	3.926
C	0.342	0.094	3.849	C	0.075	0.117	3.921
C	0.087	0.066	3.855	C	0.065	0.121	3.926
C	0.108	0.080	3.791	C	0.121	0.106	3.903
C	0.065	0.114	3.911	C	0.102	0.107	3.937
C	0.036	0.133	3.997	C	0.038	0.118	3.927
C	-0.045	0.141	3.957	C	0.117	0.109	3.909
C	0.070	0.124	3.823	C	0.091	0.067	3.833

C	0.094	0.108	3.941	C	0.264	0.087	3.936
C	0.042	0.116	3.887	C	0.109	0.105	3.911
C	0.123	0.106	3.843	C	0.043	0.118	3.937
C	0.120	0.107	3.903	C	0.085	0.070	3.845
O	-0.501	0.154	2.221	O	-0.509	0.139	2.158
O	-0.502	0.139	2.187	O	-0.489	0.160	2.168
O	-0.462	0.141	2.241	O	-0.477	0.152	2.195
O	-0.517	0.130	2.181	O	-0.313	0.175	2.442
O	-0.313	0.166	2.460	O	-0.312	0.152	2.422
O	-0.506	0.139	2.156	O	-0.507	0.135	2.167
O	-0.460	0.161	2.203	O	-0.520	0.137	2.172
O	-0.518	0.134	2.176	O	-0.522	0.134	2.176
O	-0.340	0.150	2.417	O	-0.521	0.140	2.255
O	-0.495	0.137	2.167	O	-0.495	0.136	2.202
O	-0.380	0.141	2.555	O	-0.320	0.125	2.503

SI-Table 3.2-3. NACs (q), in q_e , DMs (P), in at. units, and BOs (B) for atoms of the nominal sucrose s3 and trehalose t3 molecules.

sucrose s3				trehalose t3			
Atoms of s1	q	P	B	Atoms of t1	q	P	B
$H_1^{O(C)}$	0.360	0.041	0.898	$H_1^{O(C)}$	0.342	0.041	0.923
$H_2^{O(C)}$	0.360	0.044	0.886	$H_2^{O(C)}$	0.363	0.040	0.893
$H_3^{O(C)}$	0.325	0.023	0.992	$H_3^{O(C)}$	0.337	0.032	0.944
$H_4^{O(C)}$	0.352	0.042	0.889	$H_4^{O(C)}$	0.369	0.043	0.884
$H_5^{O(C)}$	0.363	0.042	0.892	$H_5^{O(C)}$	0.355	0.041	0.904
$H_6^{O(C)}$	0.337	0.033	0.956	$H_6^{O(C)}$	0.361	0.043	0.883
$H_7^{O(C)}$	0.339	0.041	0.920	$H_7^{O(C)}$	0.362	0.042	0.893
$H_8^{O(C)}$	0.347	0.042	0.910	$H_8^{O(C)}$	0.350	0.030	0.959
$H_9^{C(CCO)}$	0.041	0.052	0.962	$H_9^{C(CCO)}$	0.042	0.052	0.962
$H_{10}^{C(CCO)}$	0.050	0.055	0.955	$H_{10}^{C(CCO)}$	0.063	0.053	0.949
$H_{11}^{C(CCO)}$	0.065	0.051	0.933	$H_{11}^{C(CCO)}$	0.080	0.053	0.931
$H_{12}^{C(CCO)}$	0.075	0.052	0.932	$H_{12}^{C(CCO)}$	0.057	0.056	0.950
$H_{13}^{C(CCO)}$	0.058	0.054	0.954	$H_{13}^{C(CCO)}$	0.051	0.051	0.945
$H_{14}^{C(CCO)}$	0.078	0.048	0.935	$H_{14}^{C(CCO)}$	0.042	0.050	0.953
$H_{15}^{C(CCO)}$	0.041	0.050	0.951	$H_{15}^{C(CCO)}$	0.038	0.049	0.957
$H_{16}^{C(COH)}$	0.044	0.045	0.987	$H_{16}^{C(COH)}$	0.063	0.054	0.951
$H_{17}^{C(COH)}$	0.098	0.052	0.937	$H_{17}^{C(COH)}$	0.048	0.042	0.970
$H_{18}^{C(COH)}$	0.096	0.048	0.932	$H_{18}^{C(COH)}$	0.058	0.047	0.968
$H_{19}^{C(COH)}$	0.110	0.048	0.932	$H_{19}^{C(COH)}$	0.093	0.050	0.942
$H_{20}^{C(COH)}$	0.070	0.045	0.968	$H_{20}^{C(COH)}$	0.063	0.047	0.959
$H_{21}^{C(COH)}$	0.051	0.043	0.968	$H_{21}^{C(COO)}$	0.055	0.071	0.938
$H_{22}^{C(COO)}$	0.041	0.065	0.996	$H_{22}^{C(COO)}$	0.049	0.071	0.948
C	0.273	0.092	3.924	C	0.274	0.101	3.919

C	0.329	0.091	3.883	C	0.086	0.115	3.919
C	0.089	0.066	3.846	C	0.055	0.115	3.923
C	0.102	0.069	3.831	C	0.104	0.107	3.911
C	0.070	0.115	3.924	C	0.097	0.106	3.951
C	0.035	0.124	3.955	C	0.046	0.117	3.902
C	-0.030	0.137	3.928	C	0.118	0.107	3.914
C	0.051	0.125	3.893	C	0.086	0.066	3.845
C	0.094	0.108	3.937	C	0.275	0.081	3.913
C	0.045	0.117	3.924	C	0.111	0.108	3.914
C	0.119	0.109	3.909	C	0.047	0.118	3.935
C	0.124	0.106	3.903	C	0.093	0.066	3.828
O	-0.483	0.158	2.165	O	-0.508	0.141	2.159
O	-0.487	0.135	2.195	O	-0.495	0.159	2.163
O	-0.487	0.156	2.169	O	-0.488	0.150	2.233
O	-0.505	0.132	2.174	O	-0.303	0.168	2.451
O	-0.339	0.175	2.453	O	-0.321	0.169	2.424
O	-0.509	0.138	2.158	O	-0.528	0.131	2.186
O	-0.451	0.156	2.211	O	-0.523	0.133	2.179
O	-0.523	0.136	2.178	O	-0.523	0.141	2.163
O	-0.347	0.154	2.440	O	-0.501	0.135	2.175
O	-0.510	0.138	2.195	O	-0.499	0.141	2.174
O	-0.357	0.123	2.492	O	-0.345	0.134	2.472

SI-Table 3.2-4. NACs (q), in q_e , DMs (P), in at. units, and BOs (B) for the dehydrogenated and deprotonated sucrose s1, with the vacancy at the position of hydrogen atom H₉.

dehydrogenated sucrose s1 (vacancy $vH_9^{C(CCO)}$)				deprotonated sucrose s1 (vacancy $vP_9^{C(CCO)}$)			
Atoms of s1	q	P	B	Atoms of s1	q	P	B
$vH_1^{O(C)}$	0.367	0.042	0.887	$vH_1^{O(C)}$	0.360	0.040	0.899
$vH_2^{O(C)}$	0.375	0.042	0.855	$vH_2^{O(C)}$	0.320	0.049	0.959
$vH_3^{O(C)}$	0.348	0.027	0.965	$vH_3^{O(C)}$	0.339	0.025	0.989
$vH_4^{O(C)}$	0.359	0.041	0.882	$vH_4^{O(C)}$	0.346	0.039	0.902
$vH_5^{O(C)}$	0.360	0.041	0.895	$vH_5^{O(C)}$	0.348	0.039	0.919
$vH_6^{O(C)}$	0.345	0.038	0.924	$vH_6^{O(C)}$	0.271	0.026	1.035
$vH_7^{O(C)}$	0.335	0.029	0.980	$vH_7^{O(C)}$	0.333	0.023	1.004
$vH_8^{O(C)}$	0.312	0.018	1.025	$vH_8^{O(C)}$	0.319	0.022	1.012
$vH_9^{C(CCO)}$	-	-	-	$vH_9^{C(CCO)}$	-	-	-
$vH_{10}^{C(CCO)}$	0.053	0.054	0.947	$vH_{10}^{C(CCO)}$	0.059	0.056	0.955
$vH_{11}^{C(CCO)}$	0.056	0.041	0.936	$vH_{11}^{C(CCO)}$	-0.014	0.026	0.990
$vH_{12}^{vC(CCO)}$	0.048	0.051	0.951	$vH_{12}^{vC(CCO)}$	0.038	0.046	0.960
$vH_{13}^{C(CCO)}$	0.059	0.052	0.959	$vH_{13}^{C(CCO)}$	0.062	0.051	0.975
$vH_{14}^{C(CCO)}$	0.067	0.040	0.948	$vH_{14}^{C(CCO)}$	0.010	0.016	0.990
$vH_{15}^{C(CCO)}$	0.044	0.050	0.947	$vH_{15}^{C(CCO)}$	0.030	0.046	0.962
$vH_{16}^{C(COH)}$	0.085	0.049	0.943	$vH_{16}^{C(COH)}$	0.067	0.046	0.961
$vH_{17}^{C(COH)}$	0.096	0.051	0.947	$vH_{17}^{C(COH)}$	0.075	0.049	0.960

$\nu H_{18}^{C(COH)}$	0.054	0.044	0.968	$\nu H_{18}^{C(COH)}$	0.009	0.036	1.004
$\nu H_{19}^{C(COH)}$	0.109	0.050	0.940	$\nu H_{19}^{C(COH)}$	0.097	0.045	0.949
$\nu H_{20}^{C(COH)}$	0.072	0.045	0.967	$\nu H_{20}^{C(COH)}$	0.054	0.036	0.996
$\nu H_{21}^{C(COH)}$	0.049	0.043	0.970	$\nu H_{21}^{C(COH)}$	0.030	0.040	0.982
$\nu H_{22}^{C(COO)}$	0.041	0.071	0.982	$\nu H_{22}^{C(COO)}$	0.030	0.0672	0.996
C1	0.267	0.101	3.898	C1	0.254	0.100	3.959
C2	0.341	0.079	3.872	C2	0.348	0.088	3.830
C3	0.095	0.070	3.803	C3	0.089	0.073	3.812
C4	0.079	0.082	3.949	C4	0.148	0.064	3.919
C5	0.074	0.116	3.942	C5	0.081	0.119	3.936
C6	0.044	0.133	3.944	C6	0.055	0.135	3.934
C7	-0.038	0.138	3.914	C7	-0.037	0.131	3.906
C8	0.016	0.131	4.027	C8	0.095	0.118	4.017
C9	0.109	0.109	3.926	C9	0.106	0.106	3.890
C10	0.044	0.124	3.935	C10	0.060	0.124	3.952
C11	0.122	0.114	3.843	C11	-0.300	0.367	3.917
C12	0.117	0.106	3.916	C12	0.122	0.107	3.887
O1	-0.494	0.154	2.319	O1	-0.505	0.158	2.305
O2	-0.498	0.134	2.168	O2	-0.543	0.152	2.233
O3	-0.499	0.156	2.194	O3	-0.531	0.161	2.218
O4	-0.396	0.119	2.284	O4	-0.536	0.192	2.348
O5	-0.311	0.156	2.453	O5	-0.313	0.159	2.454
O6	-0.507	0.136	2.169	O6	-0.521	0.145	2.168
O7	-0.459	0.161	2.243	O7	-0.476	0.170	2.231
O8	-0.523	0.139	2.169	O8	-0.545	0.150	2.161
O9	-0.342	0.167	2.400	O9	-0.361	0.182	2.384
O10	-0.519	0.135	2.217	O10	-0.542	0.146	2.197
O11	-0.356	0.128	2.487	O11	-0.333	0.118	2.503

SI-Table 3.2-5. NACs (q), in q_e , DMs (P), in at. units, and BOs (B) for the dehydrogenated and deprotonated sucrose s2, with the vacancy at the position of hydrogen atom H₉.

dehydrogenated sucrose s2 (vacancy $\nu H_9^{C(CCO)}$)				deprotonated sucrose s2 (vacancy $\nu H_9^{C(CCO)}$)			
Atoms of s2	q	P	B	Atoms of s2	q	P	B
$\nu H_1^{O(C)}$	0.361	0.041	0.892	$\nu H_1^{O(C)}$	0.336	0.025	0.954
$\nu H_2^{O(C)}$	0.391	0.046	0.827	$\nu H_2^{O(C)}$	0.371	0.042	0.859
$\nu H_3^{O(C)}$	0.345	0.040	0.917	$\nu H_3^{O(C)}$	0.369	0.019	0.984
$\nu H_4^{O(C)}$	0.343	0.039	0.914	$\nu H_4^{O(C)}$	0.336	0.036	0.941
$\nu H_5^{O(C)}$	0.366	0.042	0.884	$\nu H_5^{O(C)}$	0.351	0.041	0.911
$\nu H_6^{O(C)}$	0.340	0.035	0.947	$\nu H_6^{O(C)}$	0.335	0.029	0.987
$\nu H_7^{O(C)}$	0.349	0.038	0.907	$\nu H_7^{O(C)}$	0.339	0.032	0.939
$\nu H_8^{O(C)}$	0.329	0.021	1.006	$\nu H_8^{O(C)}$	0.324	0.021	1.013
$\nu H_9^{C(CCO)}$	-	-	-	$\nu H_9^{C(CCO)}$	-	-	-
$\nu H_{10}^{C(CCO)}$	0.036	0.052	0.966	$\nu H_{10}^{C(CCO)}$	0.026	0.046	0.9826

$\nu H_{11}^{C(CCO)}$	0.083	0.051	0.924	$\nu H_{11}^{C(CCO)}$	0.059	0.046	0.939
$\nu H_{12}^{VC(CCO)}$	0.087	0.055	0.920	$\nu H_{12}^{VC(CCO)}$	-0.007	0.034	0.985
$\nu H_{13}^{C(CCO)}$	0.046	0.050	0.987	$\nu H_{13}^{C(CCO)}$	0.039	0.047	0.999
$\nu H_{14}^{C(CCO)}$	0.080	0.050	0.942	$\nu H_{14}^{C(CCO)}$	0.062	0.040	1.001
$\nu H_{15}^{C(CCO)}$	0.048	0.051	0.945	$\nu H_{15}^{C(CCO)}$	0.029	0.044	0.970
$\nu H_{16}^{C(COH)}$	0.043	0.044	0.990	$\nu H_{16}^{C(COH)}$	0.049	0.045	0.997
$\nu H_{17}^{C(COH)}$	0.102	0.052	0.937	$\nu H_{17}^{C(COH)}$	0.084	0.048	0.951
$\nu H_{18}^{C(COH)}$	0.083	0.050	0.941	$\nu H_{18}^{C(COH)}$	0.064	0.044	0.963
$\nu H_{19}^{C(COH)}$	0.100	0.047	0.938	$\nu H_{19}^{C(COH)}$	0.096	0.045	0.946
$\nu H_{20}^{C(COH)}$	0.064	0.045	0.971	$\nu H_{20}^{C(COH)}$	0.048	0.038	0.987
$\nu H_{21}^{C(COH)}$	0.066	0.045	0.954	$\nu H_{21}^{C(COH)}$	0.050	0.040	0.968
$\nu H_{22}^{C(COO)}$	0.064	0.073	0.960	$\nu H_{22}^{C(COO)}$	0.043	0.068	0.984
C1	0.271	0.097	3.893	C1	0.271	0.092	3.863
C2	0.341	0.093	3.865	C2	0.428	0.067	3.882
C3	0.085	0.064	3.871	C3	0.093	0.070	3.868
C4	0.060	0.092	3.937	C4	0.089	0.092	3.896
C5	0.066	0.115	3.907	C5	0.095	0.107	4.128
C6	0.051	0.123	3.953	C6	0.042	0.123	3.964
C7	-0.041	0.143	3.963	C7	-0.028	0.127	3.918
C8	0.004	0.142	4.001	C8	-0.415	0.103	3.963
C9	0.096	0.108	3.941	C9	0.094	0.112	3.944
C10	0.041	0.115	3.890	C10	0.044	0.112	3.893
C11	0.173	0.113	3.822	C11	0.243	0.116	4.132
C12	0.121	0.108	3.911	C12	0.118	0.107	3.904
O1	-0.478	0.148	2.224	O1	-0.517	0.163	2.218
O2	-0.493	0.133	2.133	O2	-0.833	0.079	1.818
O3	-0.459	0.143	2.246	O3	-0.484	0.149	2.226
O4	-0.379	0.105	2.285	O4	-0.458	0.131	2.255
O5	-0.310	0.167	2.460	O5	-0.348	0.175	2.440
O6	-0.506	0.137	2.155	O6	-0.543	0.158	2.144
O7	-0.449	0.157	2.203	O7	-0.487	0.168	2.196
O8	-0.515	0.131	2.179	O8	-0.556	0.151	2.171
O9	-0.336	0.148	2.414	O9	-0.353	0.165	2.356
O10	-0.494	0.136	2.164	O10	-0.680	0.151	2.047
O11	-0.368	0.142	2.539	O11	-0.320	0.116	2.513

SI-Table 3.2-6. NACs (q), in q_e , DMs (P), in at. units, and BOs (B) for the dehydrogenated and deprotonated sucrose s3, with the vacancy at the position of hydrogen atom H₉.

dehydrogenated sucrose s3 (vacancy $\nu H_9^{C(CCO)}$)				deprotonated sucrose s3 (vacancy $\nu P_9^{C(CCO)}$)			
Atoms of s3	q	P	B	Atoms of s3	q	P	B
$\nu H_1^{O(C)}$	0.361	0.041	0.892	$\nu H_1^{O(C)}$	0.350	0.038	0.917
$\nu H_2^{O(C)}$	0.388	0.042	0.834	$\nu H_2^{O(C)}$	0.317	0.047	0.961
$\nu H_3^{O(C)}$	0.329	0.025	0.977	$\nu H_3^{O(C)}$	0.329	0.025	0.979
$\nu H_4^{O(C)}$	0.353	0.042	0.886	$\nu H_4^{O(C)}$	0.336	0.038	0.926

$vH_5^{O(C)}$	0.365	0.041	0.888	$vH_5^{O(C)}$	0.351	0.040	0.911
$vH_6^{O(C)}$	0.327	0.027	0.977	$vH_6^{O(C)}$	0.272	0.025	1.051
$vH_7^{O(C)}$	0.338	0.042	0.913	$vH_7^{O(C)}$	0.322	0.024	0.960
$vH_8^{O(C)}$	0.352	0.043	0.895	$vH_8^{O(C)}$	0.332	0.041	0.937
$vH_9^{C(CCO)}$	-	-	-	$vH_9^{C(CCO)}$	-	-	-
$vH_{10}^{C(CCO)}$	0.051	0.055	0.954	$vH_{10}^{C(CCO)}$	0.052	0.054	0.957
$vH_{11}^{C(CCO)}$	0.076	0.047	0.922	$vH_{11}^{C(CCO)}$	0.010	0.024	0.968
$vH_{12}^{VC(CCO)}$	0.077	0.054	0.927	$vH_{12}^{VC(CCO)}$	0.062	0.049	0.941
$vH_{13}^{C(CCO)}$	0.064	0.056	0.948	$vH_{13}^{C(CCO)}$	0.066	0.055	0.949
$vH_{14}^{C(CCO)}$	0.087	0.044	0.925	$vH_{14}^{C(CCO)}$	0.017	0.018	0.987
$vH_{15}^{C(CCO)}$	0.040	0.051	0.949	$vH_{15}^{C(CCO)}$	0.030	0.046	0.960
$vH_{16}^{C(COH)}$	0.051	0.048	0.988	$vH_{16}^{C(COH)}$	0.019	0.044	1.037
$vH_{17}^{C(COH)}$	0.101	0.052	0.935	$vH_{17}^{C(COH)}$	0.079	0.049	0.951
$vH_{18}^{C(COH)}$	0.098	0.050	0.932	$vH_{18}^{C(COH)}$	0.076	0.043	0.951
$vH_{19}^{C(COH)}$	0.111	0.050	0.929	$vH_{19}^{C(COH)}$	0.092	0.045	0.946
$vH_{20}^{C(COH)}$	0.068	0.046	0.966	$vH_{20}^{C(COH)}$	0.048	0.038	0.994
$vH_{21}^{C(COH)}$	0.052	0.044	0.968	$vH_{21}^{C(COH)}$	0.033	0.040	0.982
$vH_{22}^{C(COO)}$	0.035	0.065	1.002	$vH_{22}^{C(COO)}$	0.046	0.066	1.016
C1	0.271	0.091	3.921	C1	0.263	0.100	3.935
C2	0.342	0.081	3.867	C2	0.348	0.090	3.811
C3	0.090	0.069	3.831	C3	0.088	0.071	3.852
C4	0.060	0.084	3.956	C4	0.143	0.059	3.927
C5	0.069	0.115	3.924	C5	0.075	0.115	3.916
C6	0.041	0.122	3.950	C6	0.035	0.120	3.945
C7	-0.031	0.139	3.937	C7	-0.019	0.130	3.924
C8	0.005	0.131	4.018	C8	0.087	0.118	4.021
C9	0.092	0.107	3.944	C9	0.093	0.104	3.930
C10	0.043	0.117	3.922	C10	0.054	0.118	3.941
C11	0.171	0.104	3.807	C11	-0.323	0.401	3.944
C12	0.125	0.106	3.908	C12	0.125	0.104	3.903
O1	-0.469	0.153	2.173	O1	-0.525	0.176	2.161
O2	-0.482	0.131	2.201	O2	-0.537	0.146	2.235
O3	-0.479	0.157	2.169	O3	-0.495	0.163	2.177
O4	-0.375	0.102	2.272	O4	-0.531	0.183	2.352
O5	-0.337	0.174	2.450	O5	-0.340	0.184	2.492
O6	-0.507	0.136	2.156	O6	-0.522	0.147	2.156
O7	-0.447	0.157	2.206	O7	-0.490	0.169	2.193
O8	-0.517	0.136	2.180	O8	-0.542	0.145	2.178
O9	-0.340	0.155	2.418	O9	-0.361	0.176	2.421
O10	-0.506	0.137	2.187	O10	-0.522	0.146	2.190
O11	-0.346	0.117	2.515	O11	-0.344	0.136	2.493

SI-Table 3.2-7. NACs (q), in q_e , DMs (P), in at. units, and BOs (B) for the dehydrogenated and deprotonated trehalose t1, with the vacancy at the position of hydrogen atom H₁.

dehydrogenated trehalose t1 (vacancy $vH_1^{O(C)}$)				deprotonated trehalose t1 (vacancy $vP_1^{O(C)}$)			
Atoms of t1	q	P	B	Atoms of t1	q	P	B
$vH_1^{O(C)}$	-	-	-	$vH_1^{O(C)}$	-	-	-
$vH_2^{O(C)}$	0.361	0.042	0.885	$vH_2^{O(C)}$	0.331	0.017	1.029
$vH_3^{O(C)}$	0.359	0.042	0.888	$vH_3^{O(C)}$	0.344	0.037	0.933
$vH_4^{O(C)}$	0.361	0.041	0.893	$vH_4^{O(C)}$	0.335	0.025	0.961
$vH_5^{O(C)}$	0.365	0.042	0.892	$vH_5^{O(C)}$	0.348	0.040	0.916
$vH_6^{O(C)}$	0.339	0.041	0.925	$vH_6^{O(C)}$	0.335	0.038	0.943
$vH_7^{O(C)}$	0.367	0.042	0.884	$vH_7^{O(C)}$	0.342	0.040	0.927
$vH_8^{O(C)}$	0.361	0.041	0.895	$vH_8^{O(C)}$	0.354	0.041	0.909
$vH_9^{C(CCO)}$	0.063	0.055	0.976	$vH_9^{C(CCO)}$	0.070	0.049	1.025
$vH_{10}^{C(CCO)}$	0.054	0.054	0.953	$vH_{10}^{C(CCO)}$	0.065	0.049	0.941
$vH_{11}^{C(CCO)}$	0.062	0.056	0.943	$vH_{11}^{C(CCO)}$	0.028	0.045	0.976
$vH_{12}^{C(CCO)}$	0.055	0.054	0.952	$vH_{12}^{C(CCO)}$	0.030	0.062	0.947
$vH_{13}^{C(CCO)}$	0.047	0.052	0.949	$vH_{13}^{C(CCO)}$	0.031	0.017	1.029
$vH_{14}^{C(CCO)}$	0.041	0.050	0.954	$vH_{14}^{C(CCO)}$	0.031	0.045	0.972
$vH_{15}^{C(CCO)}$	0.058	0.053	0.972	$vH_{15}^{C(CCO)}$	0.039	0.048	0.974
$vH_{16}^{C(CCO)}$	0.084	0.041	0.928	$vH_{16}^{C(CCO)}$	0.037	0.038	0.974
$vH_{17}^{C(COH)}$	0.096	0.050	0.938	$vH_{17}^{C(COH)}$	0.081	0.047	0.952
$vH_{18}^{C(COH)}$	0.119	0.045	0.911	$vH_{18}^{C(COH)}$	0.042	0.044	0.979
$vH_{19}^{C(COH)}$	0.051	0.042	0.968	$vH_{19}^{C(COH)}$	0.040	0.040	0.975
$vH_{20}^{C(COH)}$	0.045	0.067	0.945	$vH_{20}^{C(COH)}$	0.030	0.062	0.947
$vH_{21}^{C(COO)}$	0.051	0.070	0.942	$vH_{21}^{C(COO)}$	0.052	0.068	0.954
$vH_{22}^{C(COO)}$	0.058	0.088	0.936	$vH_{22}^{C(COO)}$	0.056	0.086	3.985
C1	0.073	0.116	3.918	C1	0.097	0.114	4.091
C2	0.072	0.117	3.917	C2	0.074	0.113	3.905
C3	0.121	0.106	3.899	C3	0.115	0.107	3.903
C4	0.118	0.104	3.889	C4	0.093	0.104	3.910
C5	0.046	0.117	3.922	C5	0.050	0.114	3.929
C6	0.115	0.107	3.910	C6	0.131	0.108	3.890
C7	0.103	0.074	3.822	C7	0.071	0.075	3.800
C8	0.262	0.088	3.926	C8	0.274	0.089	3.844
C9	0.113	0.104	3.897	C9	0.093	0.111	3.951
C10	0.005	0.087	4.060	C10	0.073	0.124	3.971
C11	0.087	0.068	3.847	C11	0.096	0.070	3.858
C12	-0.494	0.133	2.172	C12	-0.515	0.147	2.170
O1	-0.278	0.187	1.660	O1	-0.560	0.175	2.184
O2	-0.499	0.164	2.165	O2	-0.517	0.166	2.159
O3	-0.305	0.162	2.410	O3	-0.314	0.181	2.427
O4	-0.334	0.172	2.436	O4	-0.347	0.177	2.438
O5	-0.509	0.138	2.161	O5	-0.541	0.156	2.146
O6	-0.525	0.134	2.173	O6	-0.539	0.144	2.181

O7	-0.527	0.135	2.171	O7	-0.555	0.148	2.166
O8	-0.497	0.138	2.202	O8	-0.523	0.146	2.156
O9	-0.500	0.138	2.202	O9	-0.654	0.141	2.096
O10	-0.311	0.131	2.524	O10	-0.340	0.147	2.512
O11	0.361	0.042	0.885	O11	0.331	0.017	1.029

SI-Table 3.2-8. NACs (q), in q_e , DMs (P), in at. units, and BOs (B) for the dehydrogenated and deprotonated trehalose t2, with the vacancy at the position of hydrogen atom H₁.

dehydrogenated trehalose t2 (vacancy $vH_1^{O(C)}$)				deprotonated trehalose t2 (vacancy $vP_1^{O(C)}$)			
Atoms of t2	q	P	B	Atoms of t2	Q	P	B
$vH_1^{O(C)}$	-	-	-	$vH_1^{O(C)}$	-	-	-
$vH_2^{O(C)}$	0.359	0.043	0.884	$vH_2^{O(C)}$	0.362	0.038	0.899
$vH_3^{O(C)}$	0.327	0.022	1.003	$vH_3^{O(C)}$	0.315	0.021	1.016
$vH_4^{O(C)}$	0.365	0.041	0.891	$vH_4^{O(C)}$	0.354	0.038	0.908
$vH_5^{O(C)}$	0.362	0.042	0.892	$vH_5^{O(C)}$	0.339	0.038	0.924
$vH_6^{O(C)}$	0.335	0.037	0.926	$vH_6^{O(C)}$	0.329	0.030	0.983
$vH_7^{O(C)}$	0.370	0.042	0.873	$vH_7^{O(C)}$	0.332	0.037	0.938
$vH_8^{O(C)}$	0.363	0.042	0.890	$vH_8^{O(C)}$	0.354	0.037	0.909
$vH_9^{C(CCO)}$	0.046	0.054	0.967	$vH_9^{C(CCO)}$	0.037	0.051	0.980
$vH_{10}^{C(CCO)}$	0.074	0.058	0.940	$vH_{10}^{C(CCO)}$	0.040	0.044	0.979
$vH_{11}^{C(CCO)}$	0.069	0.054	0.937	$vH_{11}^{C(CCO)}$	0.062	0.047	0.942
$vH_{12}^{C(CCO)}$	0.060	0.055	0.942	$vH_{12}^{C(CCO)}$	0.055	0.055	0.957
$vH_{13}^{C(CCO)}$	0.053	0.054	0.951	$vH_{13}^{C(CCO)}$	0.066	0.050	0.936
$vH_{14}^{C(CCO)}$	0.046	0.052	0.951	$vH_{14}^{C(CCO)}$	0.028	0.038	0.971
$vH_{15}^{C(CCO)}$	0.045	0.051	0.946	$vH_{15}^{C(CCO)}$	0.038	0.047	0.950
$vH_{16}^{C(CCO)}$	0.044	0.051	0.982	$vH_{16}^{C(CCO)}$	0.051	0.053	0.983
$vH_{17}^{C(COH)}$	0.081	0.042	0.928	$vH_{17}^{C(COH)}$	-0.061	0.041	1.031
$vH_{18}^{C(COH)}$	0.072	0.050	0.962	$vH_{18}^{C(COH)}$	0.067	0.048	0.968
$vH_{19}^{C(COH)}$	0.119	0.046	0.914	$vH_{19}^{C(COH)}$	-0.021	0.031	1.007
$vH_{20}^{C(COH)}$	0.083	0.046	0.941	$vH_{20}^{C(COH)}$	0.064	0.043	0.954
$vH_{21}^{C(COO)}$	0.049	0.066	0.935	$vH_{21}^{C(COO)}$	0.027	0.058	0.955
$vH_{22}^{C(COO)}$	0.037	0.064	0.949	$vH_{22}^{C(COO)}$	0.040	0.061	0.949
C1	0.268	0.092	3.925	C1	0.268	0.094	3.956
C2	0.075	0.116	3.924	C2	0.077	0.114	3.934
C3	0.065	0.123	3.933	C3	0.073	0.119	3.902
C4	0.121	0.107	3.905	C4	0.126	0.105	3.894
C5	0.107	0.107	3.926	C5	0.102	0.107	3.920
C6	0.041	0.118	3.920	C6	0.051	0.121	3.933
C7	0.110	0.107	3.916	C7	0.117	0.112	3.895
C8	0.108	0.076	3.804	C8	0.093	0.076	3.751
C9	0.262	0.087	3.947	C9	0.257	0.085	3.953
C10	0.109	0.106	3.917	C10	0.092	0.106	3.924
C11	0.004	0.086	4.062	C11	0.126	0.098	4.226

C12	0.084	0.071	3.847	C12	0.082	0.072	3.847
O1	-0.486	0.133	2.170	O1	-0.515	0.151	2.197
O2	-0.253	0.183	1.660	O2	-0.761	0.209	1.909
O3	-0.474	0.150	2.195	O3	-0.505	0.160	2.182
O4	-0.282	0.164	2.420	O4	-0.278	0.157	2.486
O5	-0.311	0.153	2.427	O5	-0.323	0.161	2.414
O6	-0.506	0.135	2.167	O6	-0.516	0.142	2.170
O7	-0.518	0.137	2.171	O7	-0.536	0.149	2.193
O8	-0.521	0.135	2.175	O8	-0.532	0.145	2.190
O9	-0.517	0.140	2.250	O9	-0.531	0.145	2.257
O10	-0.491	0.134	2.203	O10	-0.507	0.140	2.166
O11	-0.319	0.124	2.531	O11	-0.341	0.124	2.516

SI-Table 3.2-9. NACs (q), in q_e , DMs (P), in at. units, and BOs (B) for the dehydrogenated and deprotonated trehalose t3, with the vacancy at the position of hydrogen atom H1.

dehydrogenated trehalose t3 (vacancy $\nu H_1^{O(C)}$)				deprotonated trehalose t3 (vacancy $\nu P_1^{O(C)}$)			
Atoms of t3	q	P	B	Atoms of t3	q	P	B
$\nu H_1^{O(C)}$	-	-	-	$\nu H_1^{O(C)}$	-	-	-
$\nu H_2^{O(C)}$	0.365	0.041	0.887	$\nu H_2^{O(C)}$	0.360	0.039	0.898
$\nu H_3^{O(C)}$	0.338	0.032	0.942	$\nu H_3^{O(C)}$	0.331	0.031	0.954
$\nu H_4^{O(C)}$	0.368	0.042	0.882	$\nu H_4^{O(C)}$	0.360	0.041	0.894
$\nu H_5^{O(C)}$	0.359	0.041	0.898	$\nu H_5^{O(C)}$	0.337	0.037	0.935
$\nu H_6^{O(C)}$	0.361	0.044	0.882	$\nu H_6^{O(C)}$	0.255	0.068	1.028
$\nu H_7^{O(C)}$	0.369	0.043	0.873	$\nu H_7^{O(C)}$	0.336	0.039	0.930
$\nu H_8^{O(C)}$	0.352	0.031	0.953	$\nu H_8^{O(C)}$	0.340	0.025	0.975
$\nu H_9^{C(CCO)}$	0.048	0.054	0.959	$\nu H_9^{C(CCO)}$	0.036	0.0490	0.971
$\nu H_{10}^{C(CCO)}$	0.070	0.057	0.940	$\nu H_{10}^{C(CCO)}$	0.049	0.047	0.964
$\nu H_{11}^{C(CCO)}$	0.082	0.053	0.926	$\nu H_{11}^{C(CCO)}$	0.071	0.048	0.936
$\nu H_{12}^{C(CCO)}$	0.060	0.056	0.945	$\nu H_{12}^{C(CCO)}$	0.070	0.058	0.941
$\nu H_{13}^{C(CCO)}$	0.051	0.051	0.943	$\nu H_{13}^{C(CCO)}$	0.037	0.046	0.956
$\nu H_{14}^{C(CCO)}$	0.048	0.053	0.949	$\nu H_{14}^{C(CCO)}$	0.027	0.039	0.972
$\nu H_{15}^{C(CCO)}$	0.039	0.049	0.956	$\nu H_{15}^{C(CCO)}$	0.026	0.040	0.971
$\nu H_{16}^{C(CCO)}$	0.061	0.053	0.950	$\nu H_{16}^{C(CCO)}$	0.067	0.055	0.949
$\nu H_{17}^{C(COH)}$	0.083	0.042	0.929	$\nu H_{17}^{C(COH)}$	-0.048	0.038	1.025
$\nu H_{18}^{C(COH)}$	0.059	0.047	0.966	$\nu H_{18}^{C(COH)}$	0.033	0.034	1.002
H17							
$\nu H_{19}^{C(COH)}$	0.115	0.046	0.922	$\nu H_{19}^{C(COH)}$	-0.005	0.034	1.000
$\nu H_{20}^{C(COH)}$	0.062	0.046	0.959	$\nu H_{20}^{C(COH)}$	0.047	0.039	0.979
$\nu H_{21}^{C(COO)}$	0.060	0.072	0.932	$\nu H_{21}^{C(COO)}$	0.037	0.066	0.951
$\nu H_{22}^{C(COO)}$	0.051	0.071	0.940	$\nu H_{22}^{C(COO)}$	0.041	0.066	0.949
C1	0.267	0.099	3.923	C1	0.268	0.100	3.954
C2	0.088	0.116	3.926	C2	0.094	0.119	3.920
C3	0.054	0.116	3.929	C3	0.058	0.111	3.920
C4	0.104	0.107	3.914	C4	0.111	0.106	3.905
C5	0.099	0.106	3.946	C5	0.096	0.104	3.944

C6	0.045	0.118	3.908	C6	0.050	0.117	3.904
C7	0.111	0.105	3.916	C7	0.121	0.113	3.901
C8	0.110	0.073	3.812	C8	0.092	0.080	3.754
C9	0.277	0.080	3.912	C9	0.272	0.081	3.926
C10	0.107	0.107	3.921	C10	0.104	0.107	3.898
C11	0.001	0.089	4.062	C11	0.108	0.101	4.209
C12	0.091	0.067	3.827	C12	0.093	0.069	3.824
O1	-0.487	0.133	2.169	O1	-0.517	0.148	2.185
O2	-0.253	0.182	1.655	O2	-0.701	0.206	1.857
O3	-0.487	0.149	2.239	O3	-0.480	0.167	2.333
O4	-0.268	0.163	2.429	O4	-0.273	0.160	2.470
O5	-0.320	0.171	2.429	O5	-0.336	0.172	2.412
O6	-0.528	0.130	2.185	O6	-0.538	0.141	2.193
O7	-0.520	0.134	2.176	O7	-0.543	0.144	2.191
O8	-0.519	0.141	2.161	O8	-0.528	0.147	2.164
O9	-0.495	0.135	2.174	O9	-0.523	0.147	2.175
O10	-0.495	0.138	2.171	O10	-0.495	0.146	2.164
O11	-0.340	0.133	2.496	O11	-0.341	0.127	2.485

SI-Table 3.2-10. NAC values (in units of q_e) of the main parts of sucrose and trehalose molecules.

Molecule	Molecule part	NAC of O _{bridge}	NAC of 5-ring s1 and NAC of 6-ring ₁ t1	NAC of 6-ring s1 and NAC of 6-ring ₂ t1
s1		-0.368	0.223	0.145
t1		-0.313	0.156	0.157

II. Figures and discussions

II.1 Figures of the three conformations of sucrose and trehalose

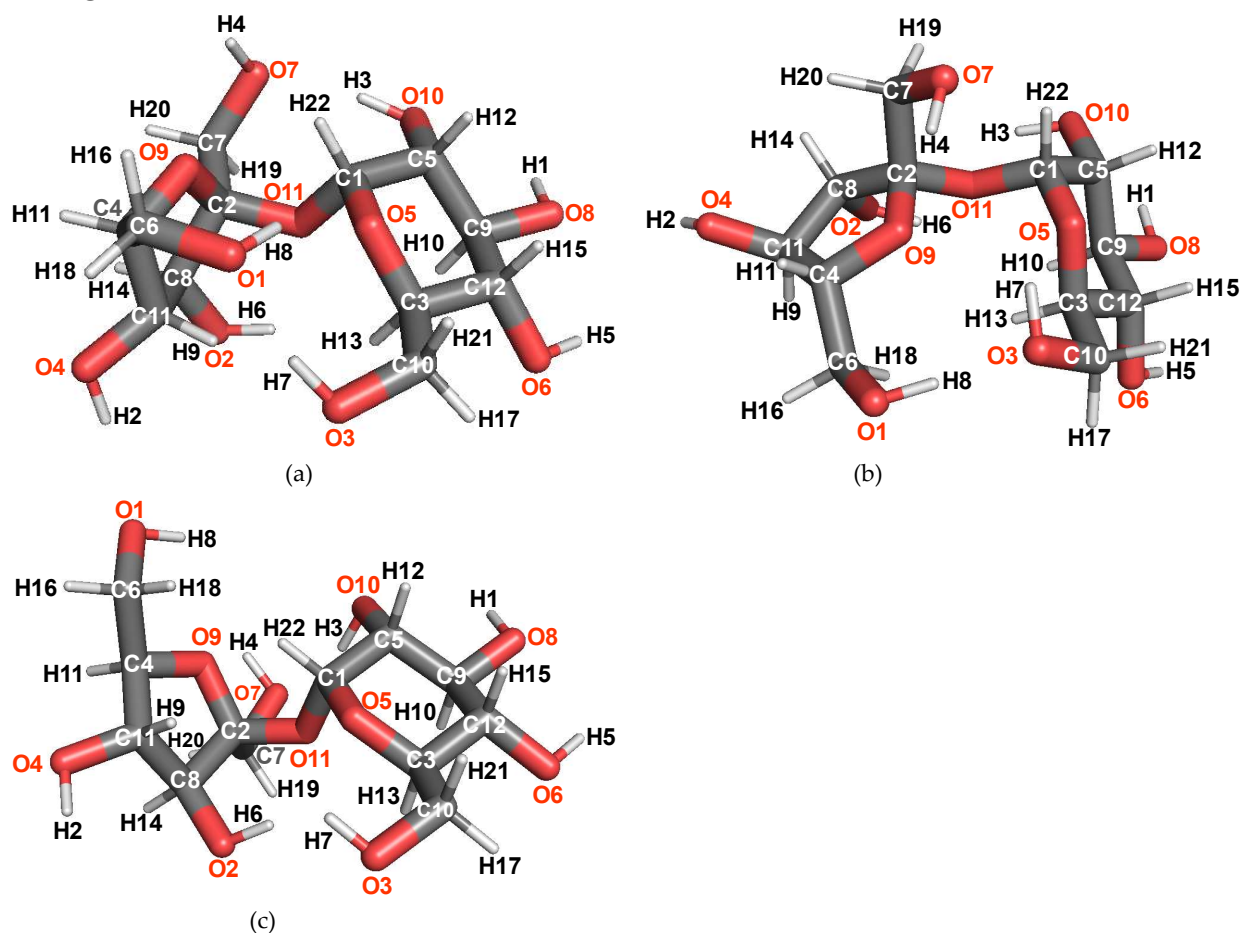


Fig. SI-1. Structures of sucrose s1 (a), sucrose s2 (b) and sucrose s3 (c). Carbon, oxygen, and hydrogen atoms are drawn in grey, red and white colors.

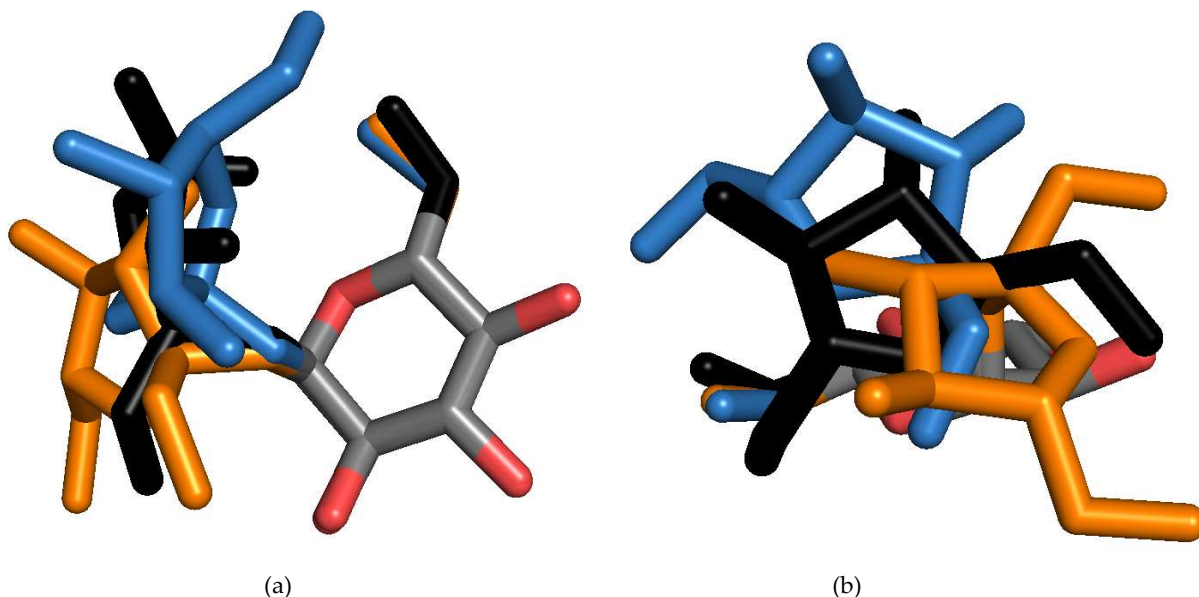


Fig. SI-2. Superimposed sucrose s1 (black), s2 (blue), and s3 (orange) structures presented from two different viewing angles, (a) and (b).

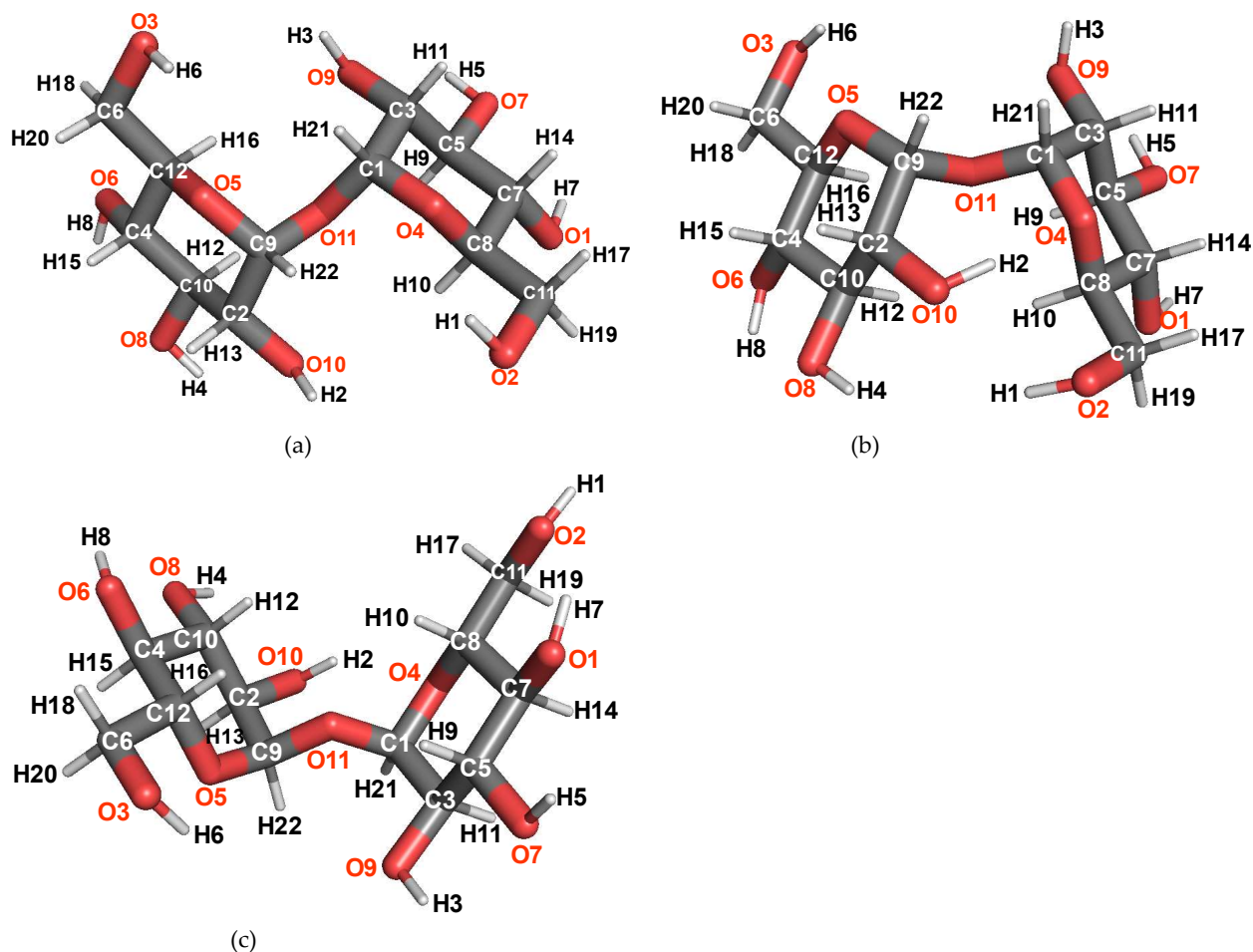


Fig. SI-3. Structures of trehalose t1 (a), trehalose t2 (b) and trehalose t3 (c). Carbon, oxygen, and hydrogen atoms are drawn in grey, red and white colors.

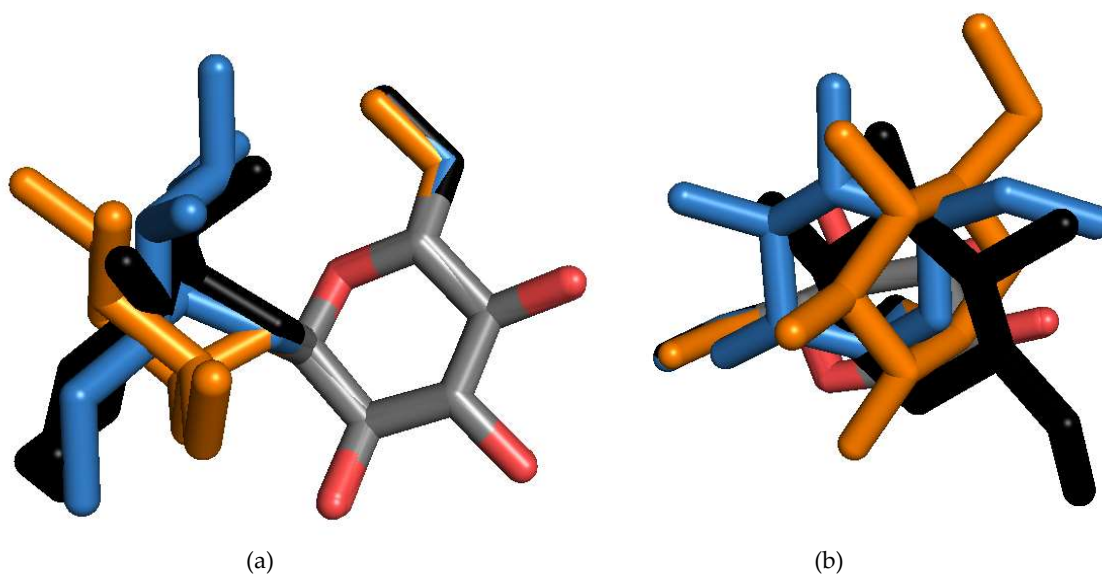


Fig. SI-4. Superimposed trehalose t1 (black), t2 (blue), and t3 (orange) structures presented from two different viewing angles, (a) and (b).

II.2 Energy calculations using the Gaussian code

In section 4.1.2 of the main text, we observe that if the proton is removed from a carbon atom, the energies of the unrelaxed deprotonated sucrose and trehalose molecules are higher than in the case when the proton has been removed from an oxygen atom. We note that we get analogous results when the Gaussian code is used for the calculations (Fig. SI-5).

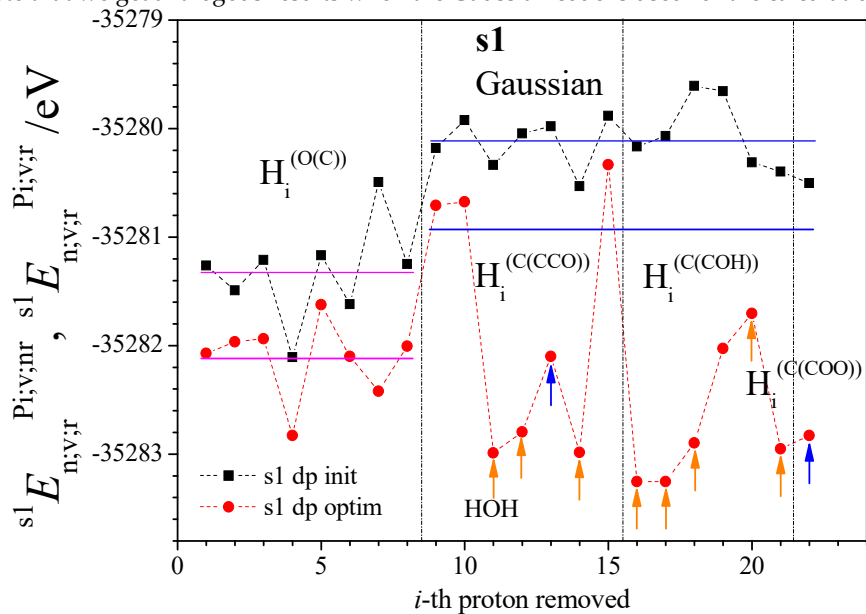


Fig. SI-5. Energies of the initial ${}^{s1}E_{n,v,r}^{Pi,v,nr}$ (black squares) and optimized states ${}^{s1}E_{n,v,r}^{Pi,v,r}$ (red circles) for deprotonated sucrose s1 as function of the i -th proton removed obtained using the Gaussian code. Horizontal lines indicate the averaged energies corresponding to the deprotonation of hydrogen atoms bonded initially to oxygen (purple) and carbon (blue) ones; only stable structures are used in these averages. Orange arrows indicate those hydrogen atoms, deprotonation of which leads to the structural destabilization and subsequent dividing of the molecule into two pieces or destruction of a 5- or 6-membered ring. Green arrows indicate those hydrogen atoms, deprotonation of which leads to the transfers to the indicated hydrogen vacancy of the nearest hydrogen atom bonded to an oxygen atom.

II.3 Electronic charges and bond analysis

In the Figs. SI-6 and SI-7 below, the NAC and BO of all hydrogen atoms for the disaccharides studied are shown, that deliver additional information to that presented in the sub-chapter 4.1.3 of the main paper. The numerical data corresponding to Figs. SI-6 and SI-7 are presented also in the form of Tables SI-3.2.1- SI-3.2.9.

It is known that the degree of ionicity (DI) of the bond between atoms A and B (DI_{A-B}) may be calculated using the empirical relation,

$$DI_{A-B} = \{1 - \exp[-0.25(X_A - X_B)^2]\},$$

where X_A and X_B are the electronegativities of atoms A and B, respectively, which are available for all elements of the periodic table [1]. Thus, the calculated values of the DI using the above formula for H-O and H-C bonds are equal to $DI_{H-O} = 0.39$ and $DI_{H-C} = 0.04$. This implies that the H-O bond exhibits ionic-covalent character, whereas the H-C one is predominantly of covalent character.

A remarkable observation is the closeness of the absolute numerical values of the NACs of the hydrogen atoms in the disaccharides and the corresponding values of the DI. Therefore, one may expect that the absolute value $|(q_{A-B}^{(ion)} - q_A^{(val)})/q_A^{(val)}|$ is close to the DI_{A-B} , mentioned above. Here, $q_{A-B}^{(ion)}$ is the NAC of atom A, $q^{(ion)}$ is the valence electron charge of the ion A in the atomic bond A - B, and $q^{(val)}$ is the valence electron charge of the neutral atom A, respectively. This seems to be reasonable because the larger the absolute value of $q_{A-B}^{(ion)} - q_A^{(val)}$ is due to the electron transfer between atoms A and B, the larger is the DI_{A-B} .

A clear difference between the NACs of the hydrogen atoms in the sucrose and trehalose molecules is observed when comparing the H-O and H-C bonds, which correlates with the different degrees of ionicity (SI-Table 3.2-1, and Fig. SI-6): the NACs are much larger when hydrogen belongs to the hydroxyl groups than when it is bonded to carbon atoms. This indicates a relatively high ionicity of the H-O bonds and a low ionicity of the H-C bonds in these molecules.

We observe a slightly larger value of the averaged NAC for hydrogen in H-O bonds for trehalose than for sucrose (Fig. SI-6), and the opposite holds true for the NACs of the hydrogen atoms in H-C bonds of trehalose and sucrose (Fig. SI-6). However, we note that the charge differences are at the limit of accuracy of the computational methods, and thus should not be over-interpreted.

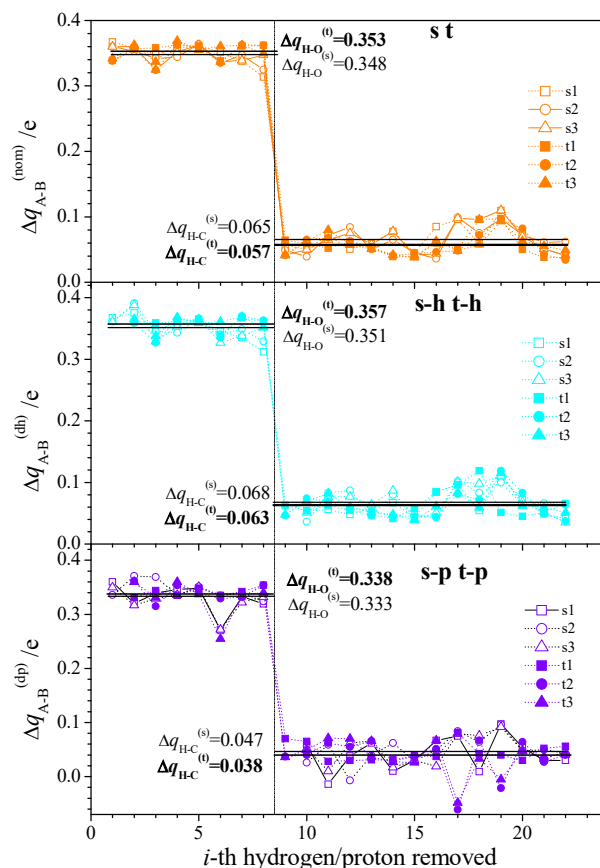


Fig. SI-6. NAC ($\Delta q_{A-B} = q_{A-B}^{(ion)} - q_A^{(val)}$) of hydrogen atoms for the nominal (nom), dehydrogenated (dh) and deprotonated (dp) sucrose and trehalose molecules. The horizontal lines indicate the averaged NACs over three disaccharide conformations (s1, s2, s3 or t1, t2, t3) and hydrogen atoms locations (H-O or H-C). Note that the average values for the trehalose and sucrose conformations are very close.

In all three forms of the disaccharides studied, nominal, dehydrogenated and deprotonated, the BOs of hydrogen atoms in the H-C bonds are larger than those in the H-O bonds (Fig. SI-7). This feature is the converse to what we saw for the corresponding NACs (Fig. SI-6), and this agrees with the intuitive interpretation that the BO mainly reflects the degree

of covalency of the bond. In most cases (Fig. SI-7), the BOs for the hydrogen atoms in sucrose are slightly larger than those for trehalose. This is in agreement with the opposite behavior of the corresponding NACs (Fig. SI-6), which depends mainly on the DI of the bond. Furthermore, we note that while the bond orders of the hydrogen atoms in the nominal and dehydrogenated molecules are quite similar (at least on average), the ones for the deprotonated molecules are considerably larger, especially for the hydrogen atoms associated with an oxygen atom. This most likely reflects the presence of the excess electron compared with the case of the dehydrogenated molecules.

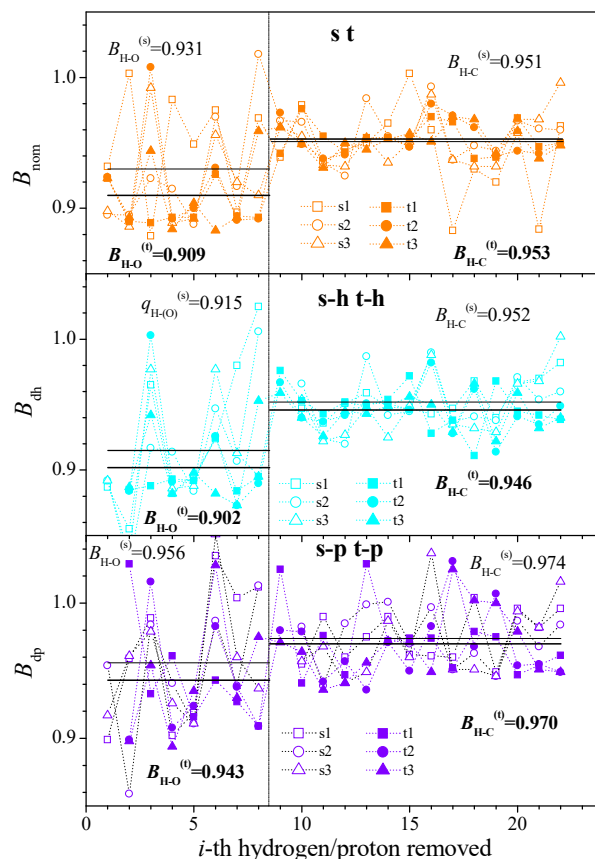


Fig. SI-7. BO (B) of hydrogen atoms for the nominal (nom), dehydrogenated (dh) and deprotonated (dp) sucrose and trehalose molecules. The horizontal lines indicate the averaged BOs over three disaccharide conformations (s1, s2, s3 or t1, t2, t3) and hydrogen atoms locations (H-O or H-C).

We also found that, for sucrose s1 and trehalose t1 molecules, the BOs of hydrogen (~ 0.94) and carbon (~ 3.91) atoms are slightly smaller (on average) than the corresponding valences of the chemical elements (1 for hydrogen and 4 for carbon), while for oxygen atoms the bond order (~ 2.26) is about 11% larger (on average) than the corresponding valence (2). The latter feature may be due to the participation of the lone electron pairs of oxygen in the interatomic bonding [2, 3]. In this context, we note that "bond order" is a rather subtle entity, whose definition employs both rigorous quantum mechanical considerations and chemical intuition, c.f. [4]. Note that what we call the bond order parameter (BO) in this study corresponds to the SBO (= Sum of Bond Orders) in the paper by Manz [4].

These considerations are also relevant for the case presented in Fig. SI-8, which concerns the transfer of two hydrogen atoms (H3 and H4). This rearrangement takes place when the optimized dehydrogenated neutral sucrose s1 structure (with the removed hydrogen atom of the type $\text{H}^{\text{C}(\text{COO})}$ from the position near to the carbon atom C1) becomes negatively charged by adding an electron; this corresponds to an effective deprotonation since we can formally visualize a deprotonation as the removal of a hydrogen atom (= proton + electron) followed by an addition of an electron. After adding the electron, the initial dehydrogenated structure becomes unstable and transforms to a new structure. During this transformation, the two hydrogen atoms (H3 and H4), which are neighbours to the initial proton vacancy $\text{dpH}^{\text{C}(\text{COO})}$ at the carbon atom, simultaneously change their positions in such a concerted way that the vacancy $\text{dpH}^{\text{C}(\text{COO})}$ moves to the nearest oxygen atom. This process corresponds to the quasi-monotonous decrease of energy of sucrose s1 found using the NEB method (Fig. SI-9).

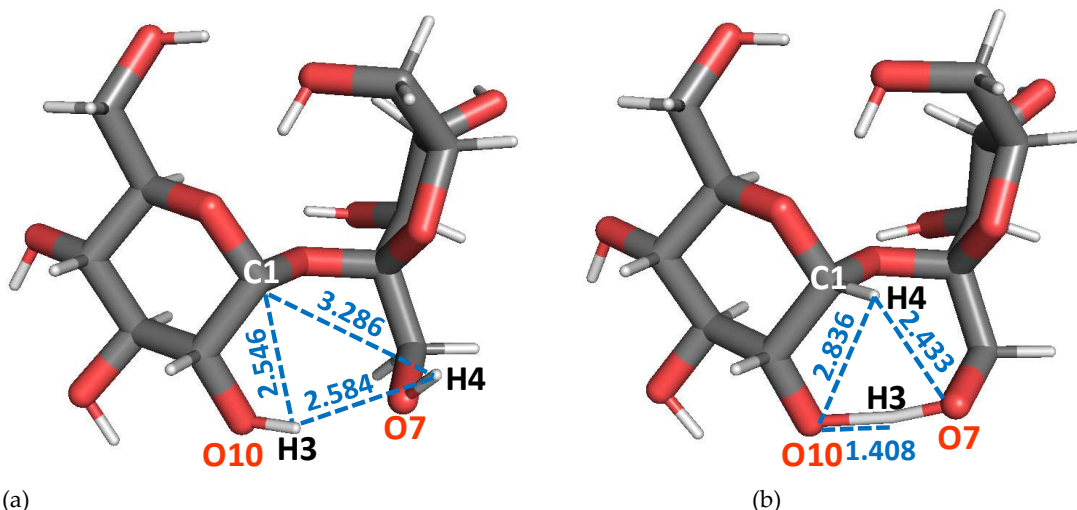


Fig. SI-8. Fragments of the atomic structure of the dehydrogenated (a) and deprotonated (b) sucrose s1. Here, the hydrogen atom $H^{C1(C5O5O11)}$ (H22) had been removed from the carbon atom C1 upon dehydrogenation/deprotonation (this is the vacancy dpH22). Interatomic distances are indicated in Angstrom.

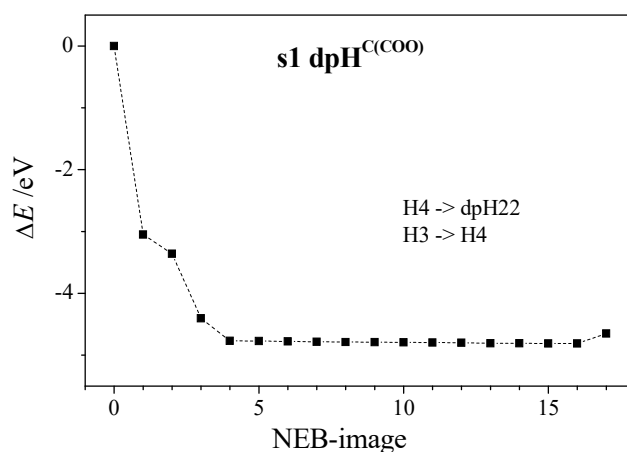
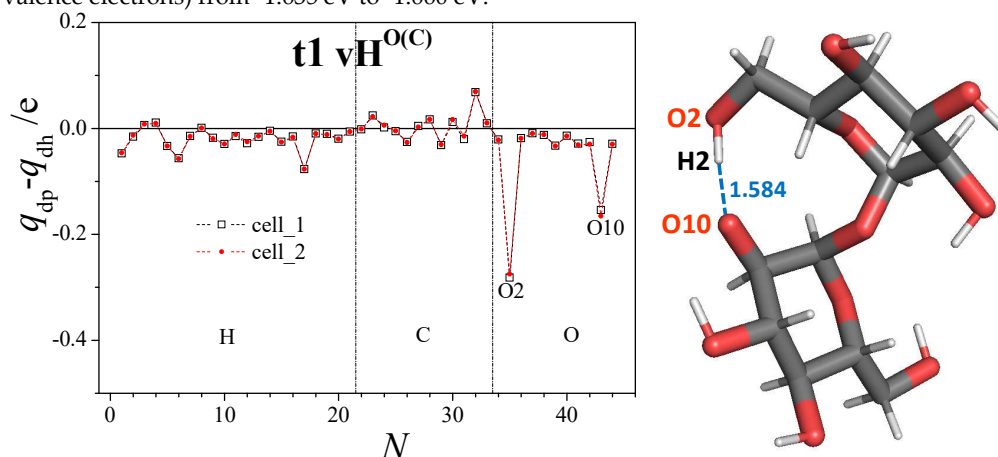


Fig. SI-9. Energy variation ΔE of the deprotonated $dpH^{C(COO)}$ sucrose s1 during the concerted transfer of H3 and H4 (see Fig. SI-8).

In contrast to the sucrose s1 molecule in Fig.8 in the main text, Fig.SI-10 presents the dehydrogenated/deprotonated trehalose t1, where the initial position of the removed hydrogen atom/proton was near the oxygen O2 atom, but where the deprotonation leads to structural changes. During the deprotonation and subsequent structure relaxation, the hydrogen atom H2 was transferred from its initial location at the oxygen atom O10 to the oxygen atom O2, and, conversely, the proton vacancy moved from O2 to O10. Deprotonation leads to the increase of the absolute values of negative charge of both neighbouring oxygen ions O2 and O10 (Fig. SI-10a). Here, the hydrogen H2 transfer (and corresponding structure optimization) is accompanied by the decrease of the specific energy (energy per number of valence electrons) from -1.635 eV to -1.660 eV.



(a) (b)
 Fig. SI-10. (a) Change of charges, $q_{dp} - q_{dh}$, for hydrogen, carbon and oxygen atoms of the deprotonated trehalose t1 compared to the dehydrogenated one in cell_1 ($V_1 = 10.7 \text{ nm}^3$) and cell_2 ($V_2 = 125 \text{ nm}^3$). (b) View of the atomic structure of deprotonated trehalose t1. Before the initial deprotonation at the oxygen atom O2, the hydrogen atom H2 of the type $\text{H}^{\text{O}(\text{C})}$ had been bonded to the oxygen atom O10. The interatomic distance is indicated in Angstrom.

Overall, we do not find large differences of NACs between sucrose and trehalose molecules: the positive NACs of hydrogen atoms are 2% larger in sucrose than in trehalose, the average positive NACs of carbon are 6% smaller in sucrose than in trehalose, and the average negative NACs of oxygen in sucrose and trehalose differ by less than 0.3%. However, we see that the negative NAC of the bridge oxygen atom is larger for sucrose s1 than for trehalose t1 (c.f. SI-Table 3.2-10). Furthermore, in sucrose s1, the average positive NAC of the five-member ring is 53% larger than the one of the six-member ring. The smaller negative charge of the five-membered ring of sucrose may cause a decrease in the structural stability of these rings when, e.g., the deprotonation occurs in this ring. It is also well-known that ring tension makes small rings more unstable than large ones. Such a structural instability with broken five-membered rings is actually observed during the deprotonation of the sucrose molecule. In contrast, in trehalose t1, the positive NACs of the two six-membered rings are almost equal. Thus, the larger asymmetry of sucrose in comparison to trehalose leads also to the larger difference in NACs of the five- and six-member rings.

For mid-sized molecules, like sucrose and trehalose, the interatomic interactions beyond nearest-neighbour atoms and their changes upon dehydrogenation and deprotonation can substantially influence the total energy of a molecule. Compared to the overall vdW interaction, the strength of the hydrogen bonds in the disaccharide molecules may be relatively large. Using the DDEC6 method we have calculated for different configurations of the disaccharides the sum of overlap populations of hydrogen and oxygen atoms. Here, we have excluded the overlap populations corresponding to the short distances $d_{\text{H-O}} \approx 1.0 \text{ \AA}$ associated with ionic/covalent H-O bonds, since they do not relate to the hydrogen bonding in the molecule. Some weak correlation between the sum of H-O overlap populations $\Pi_{\text{H-O}}$ and the total energy E can be seen in Fig. SI-11 for the dehydrogenated and deprotonated molecules. This may indicate the influence of the hydrogen bonding H-O on the overall bonding in the molecule: the larger the sum of the H-O overlap population $\Pi_{\text{H-O}}$, the larger the energy of the H-O interaction $E_{\text{H-O}}$, and thus the larger the absolute value of total energy E of the whole molecule. Following this line of argument and taking into account Fig. SI-11, one notes a trend in this influence from the neutral (nominal and dehydrogenated) to the deprotonated disaccharide.

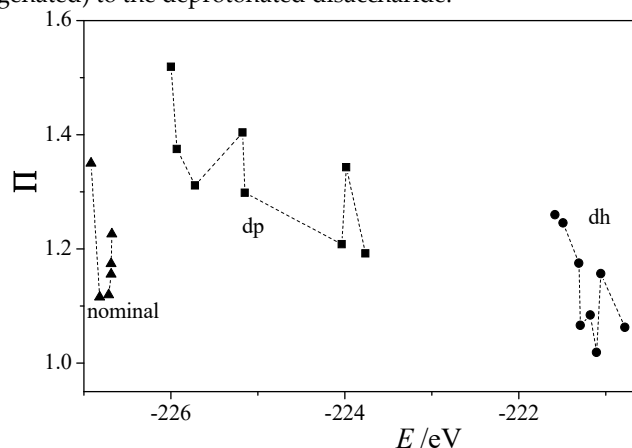


Fig. SI-11. Sum of overlap populations Π of the atom pairs H-O (excluding the eight shortest H-O distances of approximately 1 \AA , which do not contribute to hydrogen-bridge bonds) as a function of total energy E for six nominal disaccharide modifications s1, s2, s3, t1, t2, t3 (left part of the graph), eight dehydrogenated modifications (four sucrose-based plus four trehalose-based, in right part of the graph) and eight deprotonated modifications (four sucrose-based plus four trehalose-based, in middle part of the graph).

II.4 NEB calculations

As mentioned earlier, the structure where the hydrogen atom is removed from an oxygen atom has a higher specific energy than the one where the H-atom is removed from a carbon atom (Figs. 5, 6 in the main text). This means that the total energy of the relaxed dehydrogenated sucrose or trehalose molecule is minimal when the hydrogen atom is removed from one of the carbon atoms and thus all eight O-H bonds are present in the dehydrogenated molecule (this is equivalent to the fact that O-H bonds are stronger than C-H ones and the former ones deliver a larger contribution to the total energy of the molecule). As a consequence, in all those cases where the hydrogen transfer in dehydrogenated molecules occurs between an oxygen atom and a carbon atom that are direct neighbours, the structure with the transferring hydrogen atom located at the carbon atom has a higher energy than the one with the transferring hydrogen atom located at the oxygen atom (see Figs. SI-12b, c, d and Fig. SI-13a). This is true not only in relation to the total energy E (Figs. 11 and 12 in the main text) but also in relation to the specific energy E_{1e} . This specific energy allows us to compare the energies E_{1e} of the dehydrogenated and deprotonated disaccharides, which have different numbers of bonding electrons (135 and 136, respectively). One can observe a clear difference in the specific energy E_{1e} between dehydrogenated and deprotonated disaccharide molecules (Figs. SI-12b, c, d and Fig. SI-13a). The addition of one electron to the dehydrogenated disaccharide (corresponding to a deprotonation), with the hydrogen vacancy at an oxygen atom, decreases the specific energy substantially (see Figs. SI-12b, c, d, and also Fig. SI-13a for NEB images of a hydrogen atom located at carbon $H^{C(CCO)}$, for the cases of H^O to $H^{C(CCO)}$ transfers). This is probably caused by the additional electron charge localization (due to deprotonation) at the proton vacancy near the oxygen atom (this corresponds to the NEB image of a hydrogen atom localized at a carbon atom of type $H^{C(CCO)}$). The latter assumption is supported by the charges of the atoms in the deprotonated sucrose s1 obtained using the DDEC6 method (Fig. SI-6).

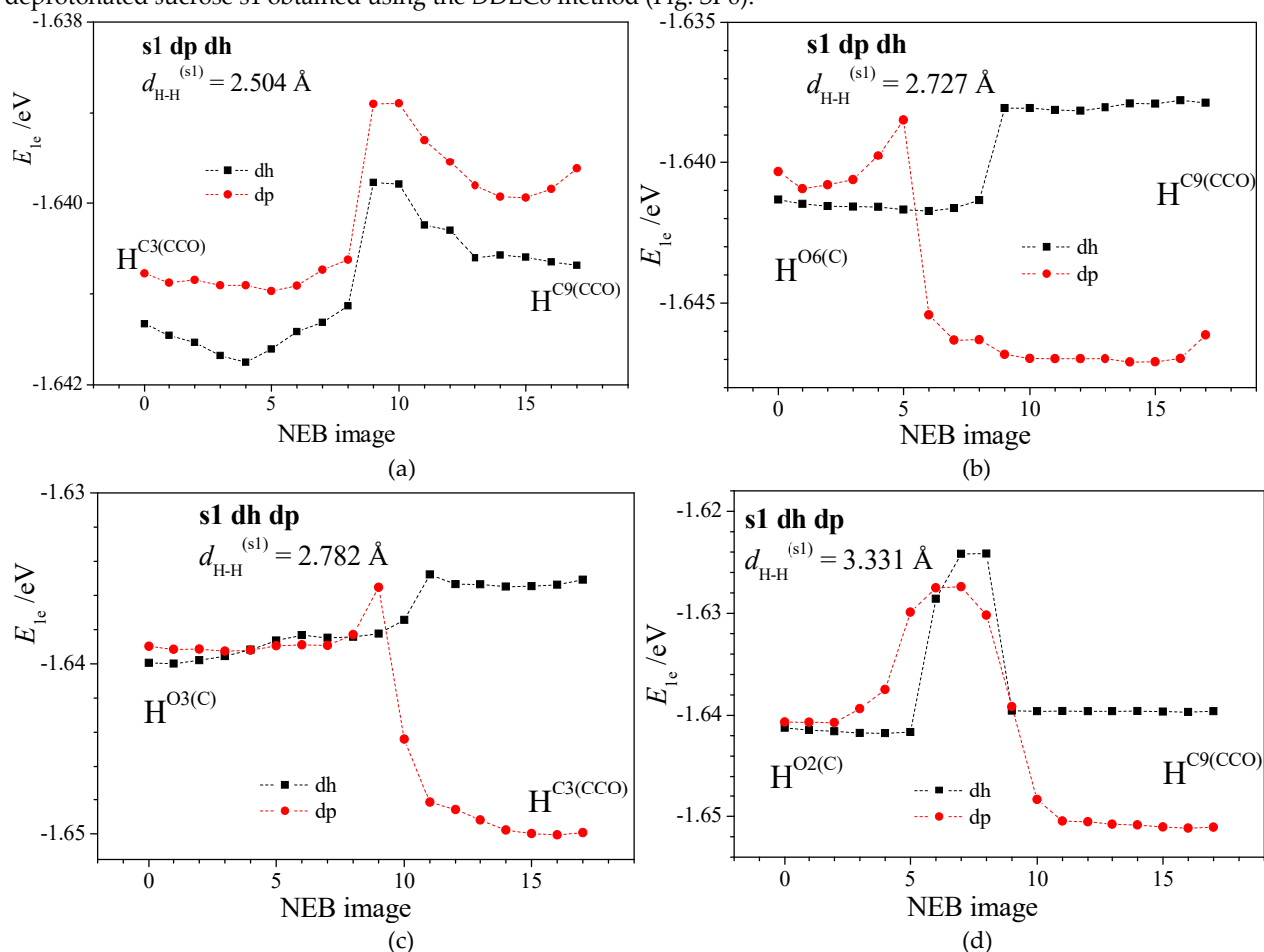


Fig. SI-12. Specific energy changes E_{1e} vs. NEB hydrogen atom images in dehydrogenated (dh) and deprotonated (dp) sucrose s1 for hydrogen transfers between different optimized positions: (a) $H^{C3(CCO)} - H^{C9(CCO)}$, (b) $H^{O6(C)} - H^{C9(CCO)}$, (c) $H^{O3(C)} - H^{C3(CCO)}$, (d) $H^{O2(C)} - H^{C9(CCO)}$. d_{H-H} is the interatomic distance H-H between hydrogen atoms in the relaxed nominal molecule, which are shifted in the NEB calculation.

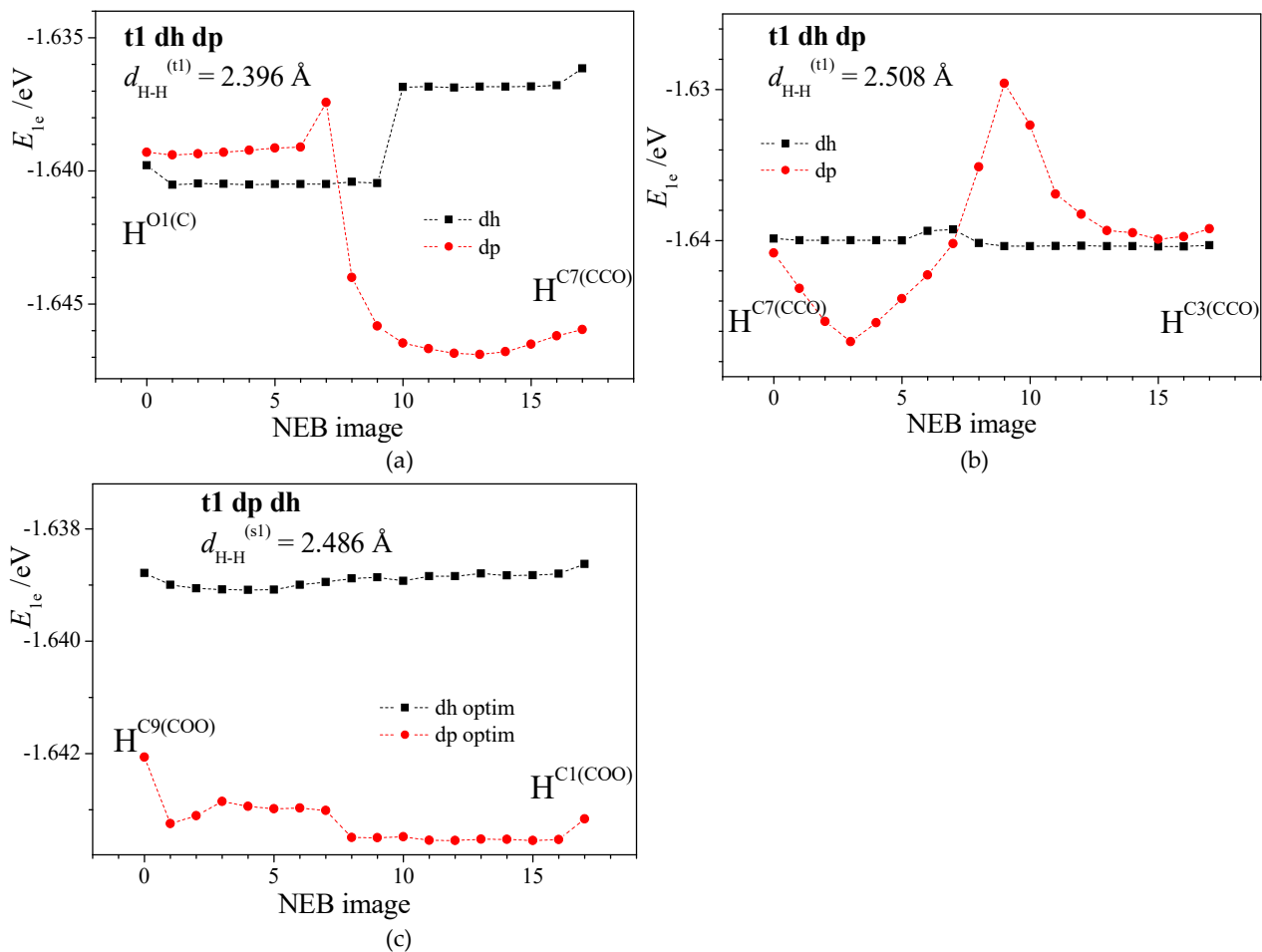


Fig. SI-13. Specific energy changes E_{1e} vs. NEB hydrogen atom images (a, b, c) in dehydrogenated (dh) and deprotonated (dp) trehalose t1 for hydrogen transfers between different optimized positions: (a) $\text{H}^{\text{O1(C)}} - \text{H}^{\text{C7(CCO)}}$, (b) $\text{H}^{\text{C7(CCO)}} - \text{H}^{\text{C3(CCO)}}$, (c) $\text{H}^{\text{C9(COO)}} - \text{H}^{\text{C1(COO)}}$. $d_{\text{H-H}}$ is the interatomic distance H-H between hydrogen atoms in the relaxed nominal molecule, which are shifted in the NEB calculation.

II.5 Radial distribution function

In figure SI-14, we show the total RDF for the three conformations of the nominal sucrose and trehalose molecules up to moderately short distances of 3 Å. We note that the very short atom-atom distances (≤ 1.6 Å), which correspond to the covalent bonds between the atoms, are essentially the same for all conformation and molecules. Even at the larger distances, the radial distributions exhibit peaks and valleys at the same positions, but with slight shifts and variations in the amplitude.

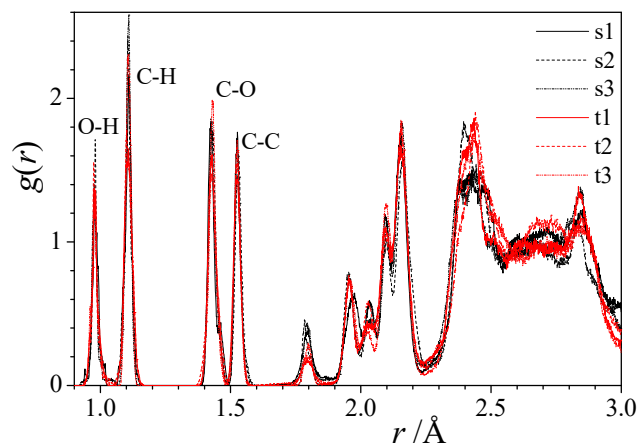


Fig. SI-14. Total RDF $g(r)$ for the nominal sucrose s1, s2, s3 and trehalose t1, t2, t3 modifications in the range of 0.9–3 Å. Note that the integrals $\int g(r)dr$ over the range of 0–3 Å has the same value for each of the six molecules [5]. The four first peaks correspond to the shortest O-H, C-H, C-O, and C-C bonds, that can be obtained from the partial (pair-wise) RDF.

II.6 Some comments on the concept of relaxation energies

After the removal of an atom or charged species from a molecular system, the remaining system is in a very high energy state, both regarding its possibly distorted structure (compared to a relaxed minimum energy structure) and with respect to its electronic state. Consequently, the system will tend to relax to a (local) minimum energy state by various mechanisms.

The classical ways of energy loss for organic systems are thermal, i.e., non-radiative. This can occur via vibrational relaxation, i.e., via what is considered in chemistry as internal conversions [6] or intersystem crossings which are radiation-less transitions from a high to a low molecular electronic state, where the energy is being transformed to heat. Note that the difference between these two mechanisms is the retention (internal conversion) or the non-retention (intersystem crossing) of the spin state.

One can also mention external conversion, in which an electronically excited molecular state relaxes to a lower one or even reaches the electronic ground state by collisions with other species of the medium. This is, for example, the mechanism involved in solvent relaxation. Another important way for the molecular system to reduce its energy is via the fragmentation of the molecule, which we have observed in a number of cases in our present study.

Of course, these non-radiative processes compete, in principle, with radiative de-excitations where a photon of the right wave length is emitted. But even in this case, the radiation based relaxation process would be accompanied by a structural adjustment of the molecule involving vibrational relaxations.

In order to avoid confusion, we note that, in physics, the term internal conversion is not only used for the analysis of chemical systems but is often also applied to the non-radiative relaxations of radioactive nuclei or of nuclear reaction products, where the energies involved are typically several orders of magnitude larger than the ones encountered in chemical systems. Here, the excitation energy of an atomic nucleus is transferred to an electron which is ejected from the atom (two other important nuclear energy relaxation pathways are the emission of gamma rays and the creation of particle-antiparticle pairs). Finally, we note the Auger effect, which describes the relaxation of a high energy state of a molecule or atom, where an energetically deep-lying electron had been ejected from an atom/molecule or moved into a high excited state, through a two-electron process where one of the valence electrons moved into the empty state and the energy associated with this transition is not released via an X-ray photon but is used to kick out another electron from the valence shell.

In the present study, we focus on energy relaxation via structural reorganization of a molecule, without or with fragmentation.

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