# Supporting Information

# Phenomenological Description of the acidity of the Citric Acid and its Deprotonated Species: Informational-Theoretical Study

Hazel Vázquez-Hernández[1], Rodolfo O. Esquivel[1,2]

October 27, 2022

[1]Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, 09340-México D.F, México

[2]Instituto *Carlos I* de Física Teórica y Computacional, Universidad de Granada 18071-Granada, Spain

# List of Figures

# List of Tables

# 1 Values for the Total Energies of the conformeric structures for the $H_2Cit^-$ and $HCit^{2-}$

| Deprotonated Acidic Hydrogen | Energy / a.u. |
|---|---|
| H1 | -759.895854 |
| H2a | -759.893263 |
| H2b | -759.893263 |

Table S1: Values of the Total Energies for the three conformeric structures of $H_2Cit^-$, following the same labeling of the acidic hydrogens of the Citric Acid depicted in Fig. 1, by use of the SMD solvent model in aqueous media, calculated at the B3LYP/6-311+g(d,p) level of theory

| Deprotonated Acidic Hydrogen | Energy / a.u. |
|---|---|
| H2a | -759.367118 |
| H2b | -759.366974 |

Table S2: Values of the Total Energies for the two conformeric structures of $HCit^{2-}$ following the same labeling of the acidic hydrogens of the Citric Acid depicted in Fig. 1, by use of the SMD solvent model in aqueous media, calculated at the B3LYP/6-311+g(d,p) level of theory.

# 2 Sensitivity analysis: method/basis-set at several levels of theory

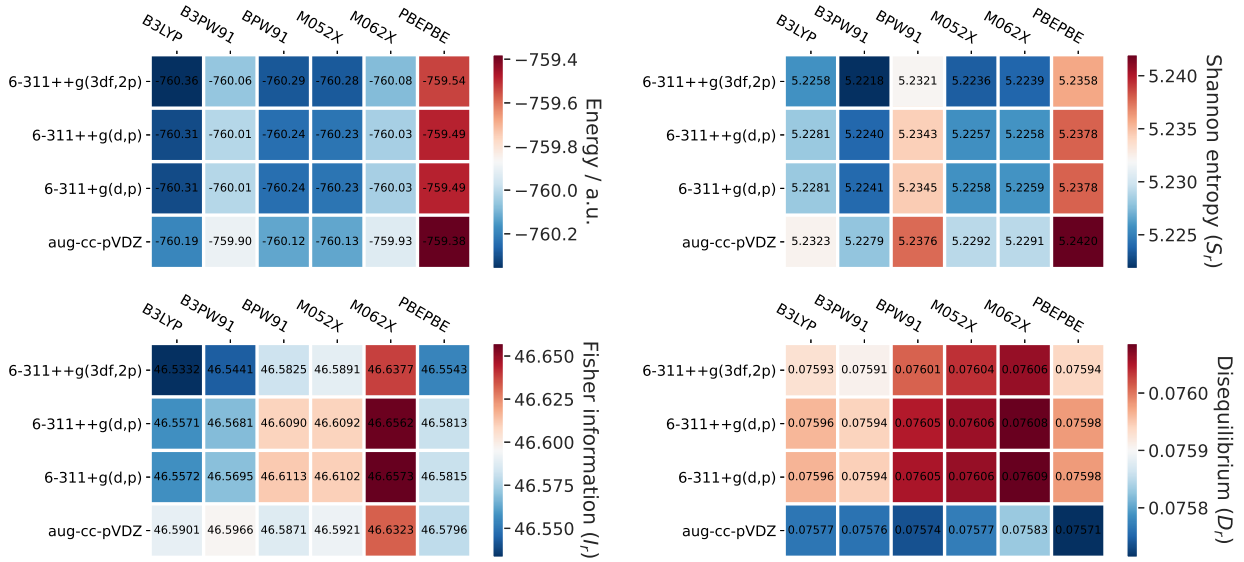



Figure S1: Energy and information-theoretic values of Shannon entropy ($S_r$), Fisher information ($I_r$) and Disequilibrium ($D_r$), calculated at different levels of theory for $H_3Cit$.

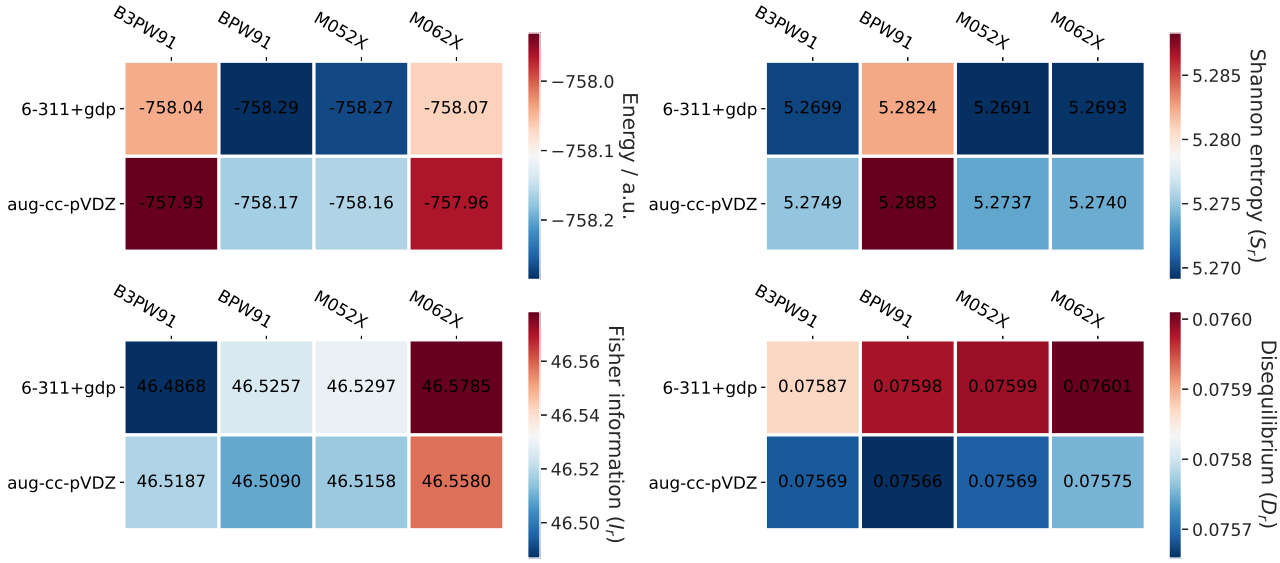



Figure S2: Energy and information-theoretic values of Shannon entropy ($S_r$), Fisher information ($I_r$) and Disequilibrium ($D_r$), calculated at different levels of theory for $Cit^{3-}$.

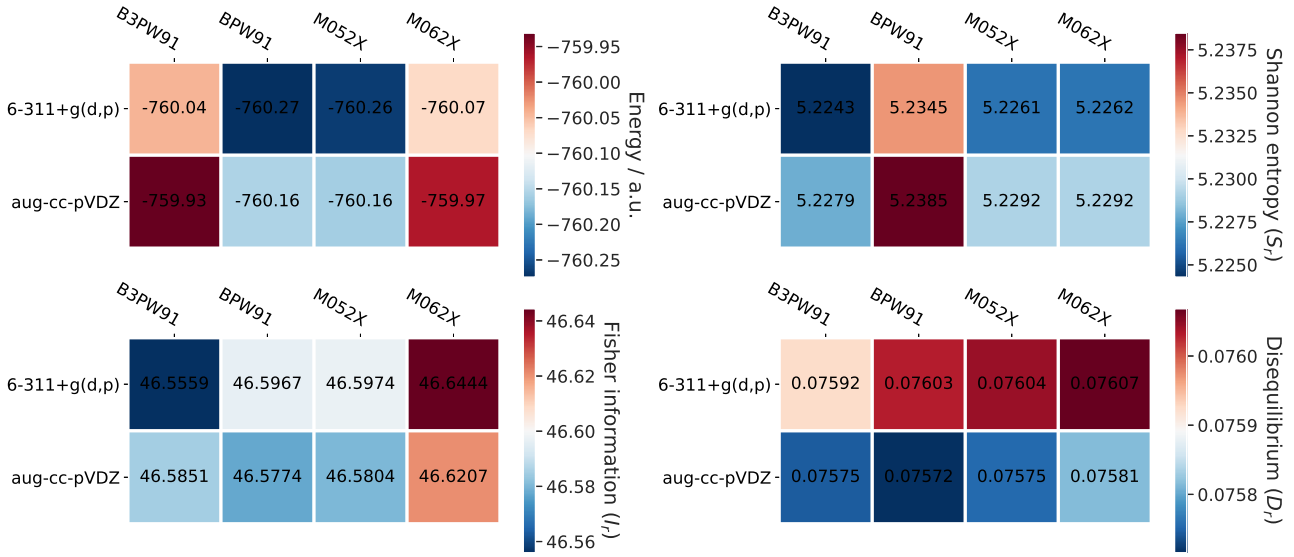



Figure S3: Energy and information-theoretic values of Shannon entropy ($S_r$), Fisher information ($I_r$) and Disequilibrium ($D_r$) by use of the *SMD* solvent model calculated at different levels of theory for $H_3Cit$ in aqueous media.

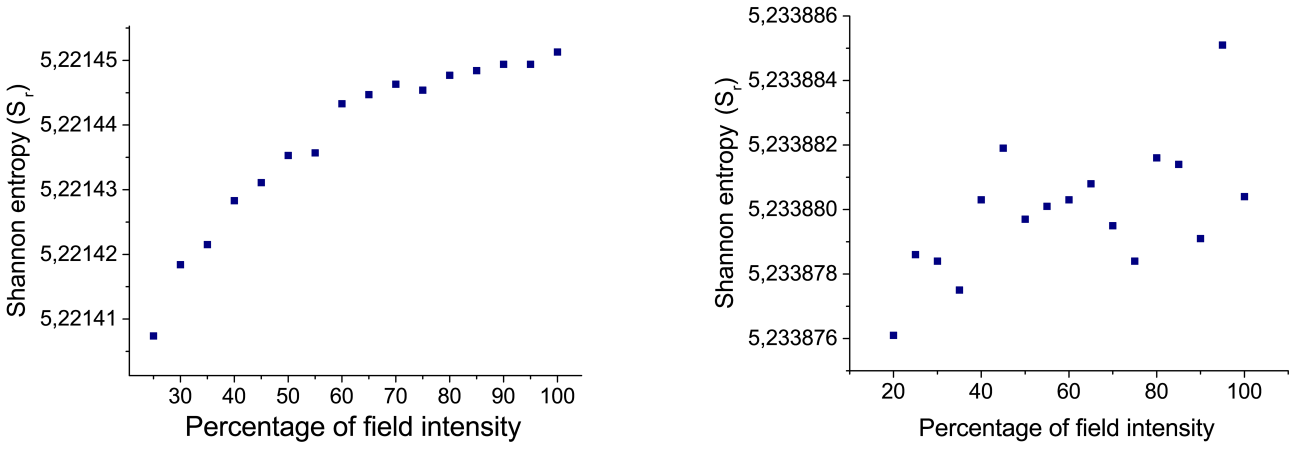
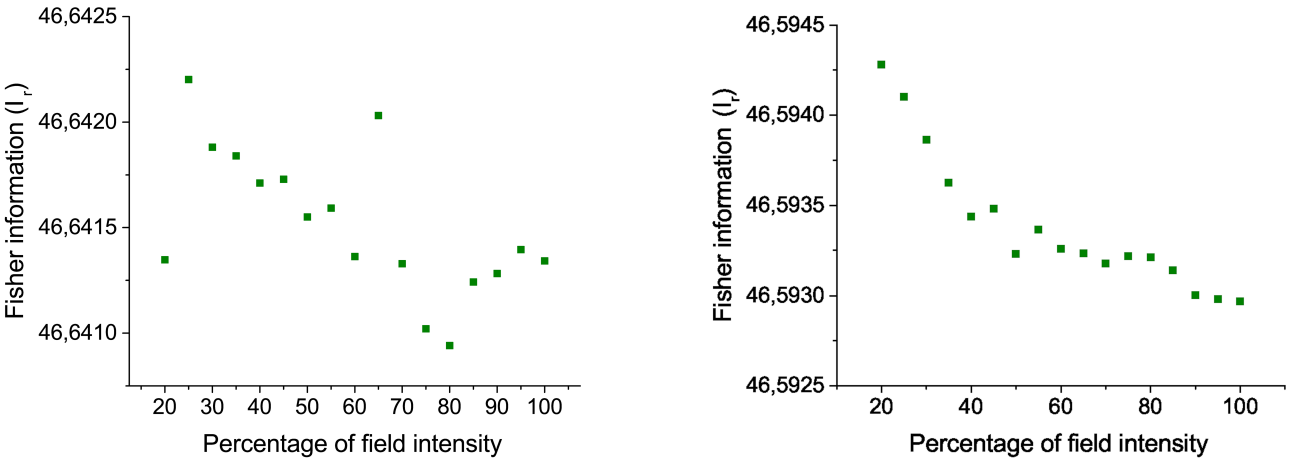
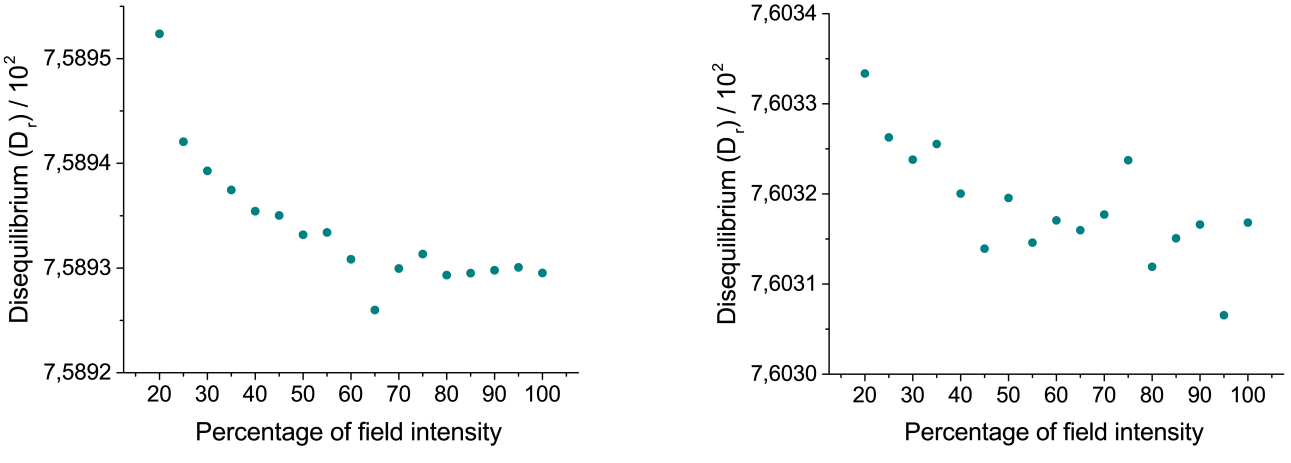



Figure S4: Shannon entropy for $H_3Cit$ as a function of the solvent's field interaction, calculated at the (a) CISD/6-311+G(d,p) and (b) BPW91/6-311+G(d,p) levels of theory, by use of Ultra Fine integration grids.




(a) (b)

Figure S5: Fisher information for $H_3Cit$ as a function of the solvent's field interaction, calculated at the (a) CISD/6-311+G(d,p) and (b) BPW91/6-311+G(d,p) levels of theory, by use of Ultra Fine integration grids.




(a) (b)

Figure S6: Disequilibrium measure for $H_3Cit$ as a function of the solvent's field interaction, calculated at the (a) CISD/6-311+G(d,p) and (b) BPW91/6-311+G(d,p) levels of theory, by use of Ultra Fine integration grids.

# 3 Tables of values for the Energies and the Information Theoretic values for water, methane, the citric acid and its deprotonated species

| %SFI | Energy / a.u. | $S_r$ | $I_r$ | $D_r$ |
|---|---|---|---|---|
| 20 | -76.45260 | 3.089031 | 45.997831 | 0.81571915 |
| 25 | -76.45293 | 3.089045 | 45.996800 | 0.81571034 |
| 30 | -76.45315 | 3.089055 | 45.996068 | 0.81570494 |
| 35 | -76.45331 | 3.089063 | 45.995566 | 0.81570061 |
| 40 | -76.45344 | 3.089069 | 45.995188 | 0.81569739 |
| 45 | -76.45353 | 3.089073 | 45.994893 | 0.81569486 |
| 50 | -76.45361 | 3.089077 | 45.994654 | 0.81569277 |
| 55 | -76.45367 | 3.089090 | 45.994371 | 0.81568760 |
| 60 | -76.45372 | 3.089083 | 45.994297 | 0.81568972 |
| 65 | -76.45377 | 3.089085 | 45.994161 | 0.81568860 |
| 70 | -76.45381 | 3.089087 | 45.994042 | 0.81568758 |
| 75 | -76.45384 | 3.089088 | 45.993940 | 0.81568671 |
| 80 | -76.45387 | 3.089090 | 45.993849 | 0.81568592 |
| 85 | -76.45389 | 3.089091 | 45.993771 | 0.81568527 |
| 90 | -76.45392 | 3.089092 | 45.993701 | 0.81568468 |
| 95 | -76.45394 | 3.089093 | 45.993637 | 0.81568414 |
| 100 | -76.45396 | 3.089094 | 45.993580 | 0.81568365 |

Table S3: Energy and information-theoretic values of Shannon entropy ($S_r$), Fisher information ($I_r$) and Disequilibrium ($D_r$) for water at different intensities (%) of the Solvent Field Interaction (SFI), calculated at the M05-2X/6-311+G(d,p) level of theory.

| %SFI | Energy / a.u. | $S_r$ | $I_r$ | $D_r$ |
|---|---|---|---|---|
| 20 | -40.51258 | 3.9700061 | 26.195913 | 0.31919939 |
| 25 | -40.51260 | 3.9700116 | 26.195758 | 0.31919905 |
| 30 | -40.51262 | 3.9700153 | 26.195652 | 0.31919881 |
| 35 | -40.51263 | 3.9700180 | 26.195576 | 0.31919864 |
| 40 | -40.51264 | 3.9700199 | 26.195519 | 0.31919852 |
| 45 | -40.51264 | 3.9700214 | 26.195474 | 0.31919842 |
| 50 | -40.51265 | 3.9700227 | 26.195438 | 0.31919834 |
| 55 | -40.51265 | 3.9700237 | 26.195409 | 0.31919828 |
| 60 | -40.51266 | 3.9700246 | 26.195383 | 0.31919819 |
| 65 | -40.51266 | 3.9700253 | 26.195362 | 0.31919816 |
| 70 | -40.51266 | 3.9700259 | 26.195345 | 0.31919813 |
| 75 | -40.51266 | 3.9700264 | 26.195329 | 0.31919808 |
| 80 | -40.51266 | 3.9700269 | 26.195315 | 0.31919805 |
| 85 | -40.51267 | 3.9700273 | 26.195303 | 0.31919803 |
| 90 | -40.51267 | 3.9700276 | 26.195292 | 0.31919801 |
| 95 | -40.51267 | 3.9700279 | 26.195283 | 0.31919800 |
| 100 | -40.51267 | 3.9700282 | 26.195274 | 0.31919797 |

Table S4: Energy and information-theoretic values of Shannon entropy ($S_r$), Fisher information ($I_r$) and Disequilibrium ($D_r$) for methane at different intensities (%) of the Solvent Field Interaction (SFI), calculated at the M05-2X/6-311+G(d,p) level of theory.

| %SFI | Energy / a.u. | $S_r$ | $I_r$ | $D_r$ |
|---|---|---|---|---|
| 20 | -760.24782 | 5.2257520 | 46.596128 | 0.07604580 |
| 25 | -760.24869 | 5.2259704 | 46.596974 | 0.07604473 |
| 30 | -760.24943 | 5.2259793 | 46.596634 | 0.07604444 |
| 35 | -760.24997 | 5.2259813 | 46.596582 | 0.07604426 |
| 40 | -760.25038 | 5.2259871 | 46.596445 | 0.07604405 |
| 45 | -760.25070 | 5.2259891 | 46.596454 | 0.07604401 |
| 50 | -760.25095 | 5.2259928 | 46.596281 | 0.07604382 |
| 55 | -760.25116 | 5.2259927 | 46.596320 | 0.07604385 |
| 60 | -760.25134 | 5.2259996 | 46.596082 | 0.07604359 |
| 65 | -760.25149 | 5.2260009 | 46.596760 | 0.07604307 |
| 70 | -760.25162 | 5.2260018 | 46.596035 | 0.07604349 |
| 75 | -760.25173 | 5.2260007 | 46.595724 | 0.07604363 |
| 80 | -760.25183 | 5.2260029 | 46.595654 | 0.07604343 |
| 85 | -760.25192 | 5.2260032 | 46.595957 | 0.07604345 |
| 90 | -760.25199 | 5.2260041 | 46.595991 | 0.07604347 |
| 95 | -760.25206 | 5.2260039 | 46.596102 | 0.07604350 |
| 100 | -760.25212 | 5.2260055 | 46.596047 | 0.07604345 |

Table S5: Energy and information-theoretic values of Shannon entropy ($S_r$), Fisher information ($I_r$) and Disequilibrium ($D_r$) for $H_3Cit$ at different intensities (%) of the Solvent Field Interaction (SFI), calculated at the M05-2X/6-311+G(d,p) level of theory.

| %SFI | Energy / a.u. | $S_r$ | $I_r$ | $D_r$ |
|---|---|---|---|---|
| 20 | -759.78871 | 5.235357 | 46.573005 | 0.07603075 |
| 25 | -759.79146 | 5.235326 | 46.572674 | 0.07603039 |
| 30 | -759.79332 | 5.235307 | 46.572449 | 0.07603013 |
| 35 | -759.79466 | 5.235293 | 46.572403 | 0.07602999 |
| 40 | -759.79567 | 5.235285 | 46.572164 | 0.07602954 |
| 45 | -759.79647 | 5.235275 | 46.572119 | 0.07602970 |
| 50 | -759.79710 | 5.235276 | 46.571988 | 0.07602949 |
| 55 | -759.79763 | 5.235271 | 46.571987 | 0.07602971 |
| 60 | -759.79806 | 5.235260 | 46.571900 | 0.07602952 |
| 65 | -759.79843 | 5.235257 | 46.571802 | 0.07602946 |
| 70 | -759.79875 | 5.235251 | 46.571841 | 0.07602971 |
| 75 | -759.79903 | 5.235250 | 46.571804 | 0.07602946 |
| 80 | -759.79927 | 5.235247 | 46.571794 | 0.07602938 |
| 85 | -759.79949 | 5.235243 | 46.571819 | 0.07602943 |
| 90 | -759.79968 | 5.235244 | 46.571656 | 0.07602929 |
| 95 | -759.79985 | 5.235239 | 46.571783 | 0.07602955 |
| 100 | -759.80000 | 5.235243 | 46.571595 | 0.07602915 |

Table S6: Energy and information-theoretic values of Shannon entropy ($S_r$), Fisher information ($I_r$) and Disequilibrium ($D_r$) for $H_2Cit^-$ at different intensities (%) of the Solvent Field Interaction (SFI), calculated at the M05-2X/6-311+G(d,p) level of theory.

| %SFI | Energy / a.u. | $S_r$ | $I_r$ | $D_r$ |
|---|---|---|---|---|
| 20 | -759.32558 | 5.243653 | 46.538456 | 0.07601304 |
| 25 | -759.33072 | 5.243579 | 46.538162 | 0.07601280 |
| 30 | -759.33418 | 5.243528 | 46.538090 | 0.07601268 |
| 35 | -759.33667 | 5.243491 | 46.537980 | 0.07601252 |
| 40 | -759.33854 | 5.243462 | 46.537910 | 0.07601256 |
| 45 | -759.34001 | 5.243440 | 46.537934 | 0.07601257 |
| 50 | -759.34118 | 5.243423 | 46.537941 | 0.07601256 |
| 55 | -759.34214 | 5.243409 | 46.537855 | 0.07601247 |
| 60 | -759.34295 | 5.243398 | 46.537790 | 0.07601242 |
| 65 | -759.34363 | 5.243386 | 46.537919 | 0.07601252 |
| 70 | -759.34421 | 5.243380 | 46.537815 | 0.07601238 |
| 75 | -759.34472 | 5.243372 | 46.537729 | 0.07601237 |
| 80 | -759.34517 | 5.243366 | 46.537621 | 0.07601232 |
| 85 | -759.34556 | 5.243362 | 46.538044 | 0.07601214 |
| 90 | -759.34591 | 5.243356 | 46.537670 | 0.07601233 |
| 95 | -759.34622 | 5.243352 | 46.537677 | 0.07601229 |
| 100 | -759.34650 | 5.243347 | 46.537683 | 0.07601230 |

Table S7: Energy and information-theoretic values of Shannon entropy ($S_r$), Fisher information ($I_r$) and Disequilibrium ($D_r$) for $HCit^{2-}$ at different intensities (%) of the Solvent Field Interaction (SFI), calculated at the M05-2X/6-311+G(d,p) level of theory.

| %SFI | Energy / a.u. | $S_r$ | $I_r$ | $D_r$ |
|---|---|---|---|---|
| 20 | -758.84910 | 5.253084 | 46.507970 | 0.07599328 |
| 25 | -758.85806 | 5.252908 | 46.507684 | 0.07599330 |
| 30 | -758.86405 | 5.252790 | 46.507593 | 0.07599375 |
| 35 | -758.86834 | 5.252704 | 46.507160 | 0.07599322 |
| 40 | -758.87156 | 5.252639 | 46.507039 | 0.07599325 |
| 45 | -758.87407 | 5.252590 | 46.506917 | 0.07599319 |
| 50 | -758.87608 | 5.252551 | 46.506810 | 0.07599320 |
| 55 | -758.87773 | 5.252519 | 46.506751 | 0.07599317 |
| 60 | -758.87910 | 5.252493 | 46.506651 | 0.07599314 |
| 65 | -758.88026 | 5.252468 | 46.506680 | 0.07599321 |
| 70 | -758.88126 | 5.252450 | 46.506626 | 0.07599320 |
| 75 | -758.88212 | 5.252433 | 46.507005 | 0.07599337 |
| 80 | -758.88288 | 5.252416 | 46.506607 | 0.07599352 |
| 85 | -758.88354 | 5.252404 | 46.506592 | 0.07599351 |
| 90 | -758.88414 | 5.252393 | 46.506534 | 0.07599320 |
| 95 | -758.88467 | 5.252382 | 46.506541 | 0.07599321 |
| 100 | -758.88515 | 5.252373 | 46.506402 | 0.07599313 |

Table S8: Energy and information-theoretic values of Shannon entropy ($S_r$), Fisher information ($I_r$) and Disequilibrium ($D_r$) for $Cit^{3-}$ at different intensities (%) of the Solvent Field Interaction (SFI), calculated at the M05-2X/6-311+G(d,p) level of theory.

# 4 Tables of values for the physicochemical properties of water, methane, the citric acid, and its deprotonated species

| %SFI | Dipole moment ($\mu$) / D | Hydrogens atomic charge / a.u. | $\Delta$AEP (O-H) / a.u. |
|---|---|---|---|
| 20 | 2.6420 | 0.47362 | 21.400839 |
| 25 | 2.6515 | 0.47507 | 21.401508 |
| 30 | 2.6580 | 0.47605 | 21.401960 |
| 35 | 2.6627 | 0.47676 | 21.402286 |
| 40 | 2.6662 | 0.47729 | 21.402533 |
| 45 | 2.6690 | 0.47771 | 21.402725 |
| 50 | 2.6712 | 0.47805 | 21.402881 |
| 55 | 2.6730 | 0.47832 | 21.403008 |
| 60 | 2.6745 | 0.47855 | 21.403114 |
| 65 | 2.6758 | 0.47875 | 21.403204 |
| 70 | 2.6769 | 0.47891 | 21.403281 |
| 75 | 2.6779 | 0.47906 | 21.403349 |
| 80 | 2.6787 | 0.47919 | 21.403408 |
| 85 | 2.6795 | 0.47930 | 21.403459 |
| 90 | 2.6801 | 0.47940 | 21.403506 |
| 95 | 2.6807 | 0.47949 | 21.403548 |
| 100 | 2.6813 | 0.47957 | 21.403585 |

Table S9: Values of the Total Dipole Moment, atomic charges (on the acidic hydrogens) and the atomic electrostatic potential (AEP) difference among the bonded atoms $O-H$ for the water molecule, calculated at the M05-2X/6-311+G(d,p) level of theory at different intensities (%) of the solvent field interaction (SFI). Note that both acidic hydrogens are equivalent

| %SFI | Hydrogens atomic charge / a.u. | ΔAEP (O-H) / a.u. |
|---|---|---|
| 20 | 0.11641 | 13.681993 |
| 25 | 0.11662 | 13.682070 |
| 30 | 0.11676 | 13.682121 |
| 35 | 0.11687 | 13.682159 |
| 40 | 0.11694 | 13.682188 |
| 45 | 0.11701 | 13.682209 |
| 50 | 0.11705 | 13.682227 |
| 55 | 0.11710 | 13.682242 |
| 60 | 0.11713 | 13.682254 |
| 65 | 0.11716 | 13.682265 |
| 70 | 0.11718 | 13.682274 |
| 75 | 0.11720 | 13.682281 |
| 80 | 0.11722 | 13.682288 |
| 85 | 0.11724 | 13.682294 |
| 90 | 0.11725 | 13.682300 |
| 95 | 0.11727 | 13.682304 |
| 100 | 0.11728 | 13.682308 |

Table S10: Values of the Total Dipole Moment, the hydrogenic atomic charges and the atomic electrostatic potential (AEP) difference among the bonded atoms $C - H$ for the methane molecule, calculated at the M05-2X/6-311+G(d,p) level of theory at different intensities (%) of the solvent field interaction (SFI). Note that all hydrogens of methane are equivalent and hence its Total Dipole Moment is null.

| %SFI | Dipole moment | Atomic charge / a.u. | | | ΔAEP / a.u. | | |
|---|---|---|---|---|---|---|---|
| | ($\mu$) / D | H1 | H2a | H2b | O-H1 | O-H2a | O-H2b |
| 20 | 4.4899 | 0.54476 | 0.50759 | 0.50973 | 21.390044 | 21.387406 | 21.382857 |
| 25 | 4.8082 | 0.54303 | 0.51040 | 0.50946 | 21.389096 | 21.387408 | 21.383630 |
| 30 | 4.7980 | 0.54478 | 0.50935 | 0.50917 | 21.389133 | 21.387440 | 21.383682 |
| 35 | 4.7879 | 0.54459 | 0.50932 | 0.50878 | 21.389164 | 21.387461 | 21.383721 |
| 40 | 4.7794 | 0.54505 | 0.50870 | 0.50863 | 21.389188 | 21.387477 | 21.383749 |
| 45 | 4.7734 | 0.54530 | 0.50882 | 0.50860 | 21.389207 | 21.387491 | 21.383770 |
| 50 | 4.7690 | 0.54509 | 0.50874 | 0.50853 | 21.389221 | 21.387503 | 21.383787 |
| 55 | 4.7658 | 0.54497 | 0.50905 | 0.50891 | 21.389232 | 21.387511 | 21.383801 |
| 60 | 4.7633 | 0.54503 | 0.50903 | 0.50889 | 21.389240 | 21.387520 | 21.383812 |
| 65 | 4.7614 | 0.54504 | 0.50910 | 0.50894 | 21.389247 | 21.387526 | 21.383821 |
| 70 | 4.7597 | 0.54478 | 0.50909 | 0.50844 | 21.389253 | 21.387531 | 21.383830 |
| 75 | 4.7581 | 0.54478 | 0.50919 | 0.50844 | 21.389258 | 21.387537 | 21.383836 |
| 80 | 4.7567 | 0.54470 | 0.50917 | 0.50847 | 21.389261 | 21.387541 | 21.383843 |
| 85 | 4.7553 | 0.54465 | 0.50912 | 0.50844 | 21.389264 | 21.387544 | 21.383849 |
| 90 | 4.7542 | 0.54460 | 0.50916 | 0.50861 | 21.389268 | 21.387547 | 21.383853 |
| 95 | 4.7531 | 0.54461 | 0.50916 | 0.50866 | 21.389269 | 21.387550 | 21.383857 |
| 100 | 4.7521 | 0.54462 | 0.50915 | 0.50864 | 21.389272 | 21.387553 | 21.383862 |

Table S11: Values of the Total Dipole Moment, the hydrogenic atomic charges (H1,H2a,H2b) and the atomic electrostatic potential (AEP) difference among the bonded atoms $O - H$ for the $H_3Cit$ acid, calculated at the M05-2X/6-311+G(d,p) level of theory at different intensities (%) of the solvent field interaction (SFI).

| %SFI | Dipole moment | Atomic charge / a.u. | | ΔAEP / a.u. | |
|---|---|---|---|---|---|
| | ($\mu$) / D | H2a | H2b | O-H2a | O-H2b |
| 20 | 8.6530 | 0.50749 | 0.50591 | 21.405407 | 21.402685 |
| 25 | 8.6827 | 0.50760 | 0.50604 | 21.405544 | 21.402832 |
| 30 | 8.7031 | 0.50768 | 0.50607 | 21.405639 | 21.402938 |
| 35 | 8.7178 | 0.50787 | 0.50612 | 21.405712 | 21.403020 |
| 40 | 8.7290 | 0.50796 | 0.50651 | 21.405771 | 21.403080 |
| 45 | 8.7380 | 0.50805 | 0.50641 | 21.405818 | 21.403129 |
| 50 | 8.7455 | 0.50804 | 0.50648 | 21.405850 | 21.403171 |
| 55 | 8.7515 | 0.50807 | 0.50653 | 21.405883 | 21.403205 |
| 60 | 8.7569 | 0.50822 | 0.50618 | 21.405941 | 21.403212 |
| 65 | 8.7611 | 0.50803 | 0.50679 | 21.405969 | 21.403235 |
| 70 | 8.7648 | 0.50805 | 0.50680 | 21.405994 | 21.403253 |
| 75 | 8.7680 | 0.50827 | 0.50698 | 21.406016 | 21.403270 |
| 80 | 8.7707 | 0.50827 | 0.50704 | 21.406036 | 21.403284 |
| 85 | 8.7732 | 0.50845 | 0.50706 | 21.406054 | 21.403297 |
| 90 | 8.7743 | 0.50850 | 0.50707 | 21.406083 | 21.403305 |
| 95 | 8.7762 | 0.50845 | 0.50714 | 21.406099 | 21.403315 |
| 100 | 8.7778 | 0.50847 | 0.50703 | 21.406114 | 21.403325 |

Table S12: Values of the Total Dipole Moment, the hydrogenic atomic charges (H2a,H2b) and the atomic electrostatic potential (AEP) difference among the bonded atoms $O-H$ for the $H_2Cit^-$ acid, calculated at the M05-2X/6-311+G(d,p) level of theory at different intensities (%) of the solvent field interaction (SFI).

| %SFI | Dipole moment | Atomic charge / a.u. | ΔAEP / a.u. |
|---|---|---|---|
| | ($\mu$) / D | H2b | O-H2b |
| 20 | 14.7346 | 0.49782 | 21.409953 |
| 25 | 14.8369 | 0.49963 | 21.410806 |
| 30 | 14.9041 | 0.50148 | 21.411311 |
| 35 | 14.9587 | 0.50254 | 21.411662 |
| 40 | 15.0029 | 0.50343 | 21.411924 |
| 45 | 15.0391 | 0.50395 | 21.412137 |
| 50 | 15.0689 | 0.50443 | 21.412308 |
| 55 | 15.0939 | 0.50478 | 21.412449 |
| 60 | 15.1151 | 0.50540 | 21.412564 |
| 65 | 15.1332 | 0.50560 | 21.412661 |
| 70 | 15.1490 | 0.50576 | 21.412743 |
| 75 | 15.1628 | 0.50587 | 21.412813 |
| 80 | 15.1750 | 0.50609 | 21.412872 |
| 85 | 15.1858 | 0.50626 | 21.412924 |
| 90 | 15.1956 | 0.50634 | 21.412968 |
| 95 | 15.2044 | 0.50650 | 21.413006 |
| 100 | 15.2125 | 0.50662 | 21.413039 |

Table S13: Values of the Total Dipole Moment, the hydrogenic atomic charge (H2b) and the atomic electrostatic potential (AEP) difference among the bonded atoms $O-H$ for the $HCit^{2-}$ acid, calculated at the M05-2X/6-311+G(d,p) level of theory at different intensities (%) of the solvent field interaction (SFI).

# 5 Geometrical values of the citric acid, and its deprotonated species

| %SFI | Bond distances / a.u. | | | Angles (O-C-O,$^{o}$) | | |
|---|---|---|---|---|---|---|
| | O-H1 | O-H2a | O-H2b | H1 | H2a | H2b |
| 20 | 0.970468 | 0.970918 | 0.970197 | 124.0273 | 122.9765 | 122.9436 |
| 25 | 0.970418 | 0.970669 | 0.970319 | 124.1254 | 122.9624 | 122.8988 |
| 30 | 0.970486 | 0.970722 | 0.970386 | 124.1465 | 122.9717 | 122.9107 |
| 35 | 0.970534 | 0.970759 | 0.970435 | 124.1665 | 122.9787 | 122.9218 |
| 40 | 0.970570 | 0.970786 | 0.970471 | 124.1821 | 122.9842 | 122.9308 |
| 45 | 0.970600 | 0.970808 | 0.970502 | 124.1927 | 122.9888 | 122.9366 |
| 50 | 0.970623 | 0.970825 | 0.970528 | 124.2003 | 122.9924 | 122.9406 |
| 55 | 0.970645 | 0.970839 | 0.970549 | 124.2059 | 122.9955 | 122.9434 |
| 60 | 0.970662 | 0.970852 | 0.970567 | 124.2103 | 122.9980 | 122.9453 |
| 65 | 0.970675 | 0.970861 | 0.970583 | 124.2138 | 123.0002 | 122.9468 |
| 70 | 0.970689 | 0.970871 | 0.970597 | 124.2168 | 123.0021 | 122.9481 |
| 75 | 0.970700 | 0.970878 | 0.970608 | 124.2195 | 123.0037 | 122.9491 |
| 80 | 0.970710 | 0.970885 | 0.970619 | 124.2218 | 123.0050 | 122.9499 |
| 85 | 0.970719 | 0.970892 | 0.970628 | 124.2238 | 123.0063 | 122.9507 |
| 90 | 0.970726 | 0.970897 | 0.970636 | 124.2256 | 123.0074 | 122.9513 |
| 95 | 0.970734 | 0.970901 | 0.970643 | 124.2272 | 123.0083 | 122.9519 |
| 100 | 0.970740 | 0.970906 | 0.970651 | 124.2286 | 123.0092 | 122.9524 |

Table S14: Values of the $O-H$ bond distances for the acidic hydrogens H1,H2a,H2b, and the $O-C-O$ angles of the carbonyl groups, after geometry optimization of the citric acid $H_3Cit$ at the M05-2X/6-311+G(d,p) level of theory at different intensities (%) of the solvent field interaction (SFI).

| %SFI | Bond distances / a.u. | | Angles (O-C-O,º) | | |
|---|---|---|---|---|---|
| | O-H2a | O-H2b | H1 | H2a | H2b |
| 20 | 0.969987 | 0.969822 | 127.23511 | 122.5625 | 122.5712 |
| 25 | 0.970112 | 0.969960 | 127.13229 | 122.5410 | 122.5490 |
| 30 | 0.970195 | 0.970050 | 127.06206 | 122.5263 | 122.5326 |
| 35 | 0.970252 | 0.970114 | 127.01072 | 122.5160 | 122.5198 |
| 40 | 0.970293 | 0.970157 | 126.97093 | 122.5084 | 122.5094 |
| 45 | 0.970316 | 0.970162 | 126.93249 | 122.5037 | 122.4967 |
| 50 | 0.970337 | 0.970180 | 126.9024 | 122.5011 | 122.4878 |
| 55 | 0.970357 | 0.970200 | 126.87886 | 122.4991 | 122.4813 |
| 60 | 0.970374 | 0.970219 | 126.859 | 122.4978 | 122.4758 |
| 65 | 0.970388 | 0.970235 | 126.84264 | 122.4966 | 122.4713 |
| 70 | 0.970401 | 0.970252 | 126.82894 | 122.4956 | 122.4676 |
| 75 | 0.970411 | 0.970266 | 126.81729 | 122.4947 | 122.4644 |
| 80 | 0.970421 | 0.970279 | 126.8072 | 122.4938 | 122.4616 |
| 85 | 0.970429 | 0.970290 | 126.79846 | 122.4932 | 122.4591 |
| 90 | 0.970437 | 0.970300 | 126.79063 | 122.4926 | 122.4569 |
| 95 | 0.970444 | 0.970309 | 126.78364 | 122.4920 | 122.4549 |
| 100 | 0.970450 | 0.970317 | 126.77743 | 122.4915 | 122.4531 |

Table S15: Values of the $O-H$ bond distances for the acidic hydrogens H2a,H2b, and the $O-C-O$ angles of the carbonyl groups, after geometry optimization of the $H_2Cit^-$ deprotonated species at the M05-2X/6-311+G(d,p) level of theory at different intensities (%) of the solvent field interaction (SFI).

| %SFI | Bond distances / a.u. | Angles (O-C-O,º) | | |
|---|---|---|---|---|
| | O-H2b | H1 | H2a | H2b |
| 20 | 0.969613 | 126.4564 | 125.2712 | 122.2051 |
| 25 | 0.969789 | 126.3604 | 125.1885 | 122.2330 |
| 30 | 0.969905 | 126.2912 | 125.1251 | 122.2559 |
| 35 | 0.969991 | 126.2464 | 125.0874 | 122.2709 |
| 40 | 0.970059 | 126.2150 | 125.0618 | 122.2804 |
| 45 | 0.970114 | 126.1912 | 125.0428 | 122.2860 |
| 50 | 0.970160 | 126.1722 | 125.0279 | 122.2894 |
| 55 | 0.970199 | 126.1569 | 125.0159 | 122.2916 |
| 60 | 0.970232 | 126.1441 | 125.0060 | 122.2932 |
| 65 | 0.970260 | 126.1334 | 124.9978 | 122.2942 |
| 70 | 0.970285 | 126.1243 | 124.9908 | 122.2950 |
| 75 | 0.970306 | 126.1164 | 124.9849 | 122.2954 |
| 80 | 0.970325 | 126.1097 | 124.9798 | 122.2956 |
| 85 | 0.970343 | 126.1036 | 124.9753 | 122.2959 |
| 90 | 0.970359 | 126.0983 | 124.9714 | 122.2959 |
| 95 | 0.970373 | 126.0937 | 124.9680 | 122.2958 |
| 100 | 0.970385 | 126.0894 | 124.9650 | 122.2957 |

Table S16: Values of the $O-H$ bond distance for the acidic hydrogen H2b, and the $O-C-O$ angles of the carbonyl groups, after geometry optimization of the $HCit^{2-}$ deprotonated species at the M05-2X/6-311+G(d,p) level of theory at different intensities (%) of the solvent field interaction (SFI).

| %SFI | Angles (O-C-O,º) | | |
|---|---|---|---|
| | H1 | H2a | H2b |
| 20 | 125.5419 | 125.03151 | 124.64492 |
| 25 | 125.50551 | 124.99266 | 124.61696 |
| 30 | 125.47325 | 124.97007 | 124.59841 |
| 35 | 125.44693 | 124.95263 | 124.58612 |
| 40 | 125.43334 | 124.93361 | 124.57666 |
| 45 | 125.42359 | 124.91773 | 124.56923 |
| 50 | 125.41627 | 124.90451 | 124.56333 |
| 55 | 125.41032 | 124.89329 | 124.55858 |
| 60 | 125.40547 | 124.88389 | 124.55453 |
| 65 | 125.40154 | 124.8758 | 124.55113 |
| 70 | 125.39816 | 124.86885 | 124.54827 |
| 75 | 125.39527 | 124.86272 | 124.54564 |
| 80 | 125.39286 | 124.85728 | 124.54349 |
| 85 | 125.39077 | 124.85253 | 124.54157 |
| 90 | 125.38881 | 124.84827 | 124.53986 |
| 95 | 125.38729 | 124.84433 | 124.53828 |
| 100 | 125.38584 | 124.84095 | 124.53686 |

Table S17: Values of the $O-C-O$ angles of the carbonyl groups, after geometry optimization of the $Cit^{3-}$ deprotonated species at the M05-2X/6-311+G(d,p) level of theory at different intensities (%) of the solvent field interaction (SFI).