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


# Substituent effects on the relaxation dynamics of furan, furfural and $\beta$-furfural: A combined theoretical and experimental approach (Electronic Supplementary Information)

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## 1 Ionization spectra of furfural

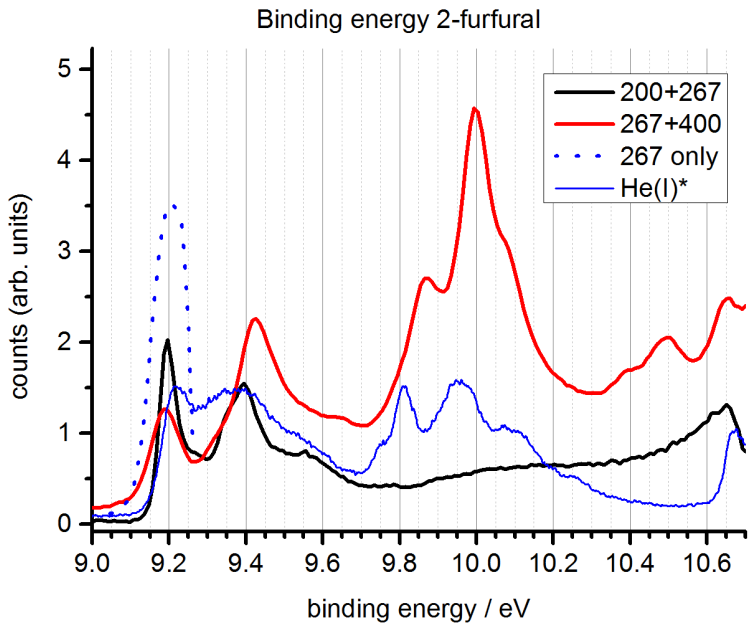


**Fig. S1** Ionization spectra at time zero for furfural upon pump-probe energies of 200+267 nm (black), 267+400 nm (red) and 267 nm only (blue dashed). Attached is a He(I) spectrum of furfural (blue curve, data as obtained from P. Limão-Vieira as published in [Jones *et al., J. Chem. Phys.*, 2015, **143**, 184310]).

## 2 Measurement of the pyramidalization

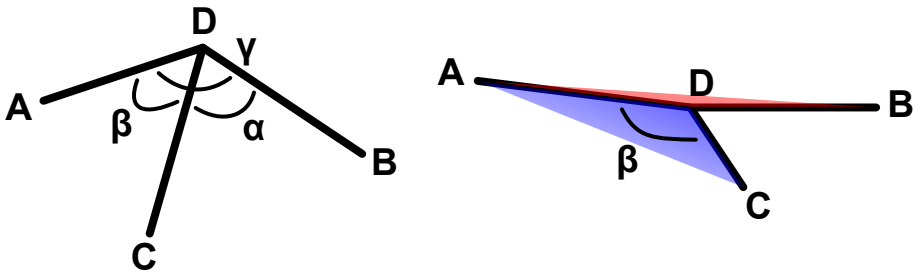


**Fig. S2** To measure the pyramidalization of a central atom (D), we use the sum of the angles between the surrounding atoms (ADB= $\gamma$, BDC= $\alpha$, CDA= $\beta$). It is independent of bondlengths and, in comparison to the dihedral angle, gives an unique value and clearer information. To receive an easy to read value, we subtract the sum from $360^\circ$ and divide by $(360^\circ - 3 * 109.471^\circ)$, the value for three times the inner angle in a tetrahedral surrounding: $(360 - (\alpha + \beta + \gamma))/31.587$. This way one runs from 0 (planar), over 1 (tetrahedral) and 2.85 ($\alpha = \beta = \gamma = 90^\circ$) to 11.40 (A, B and C are aligned). Especially in cases were A, B and C are not distributed equally around D, it produces more meaningful results, compared to the dihedral angle. As an example the right side shows the the planes considered in the dihedral angle ADCB. The closer $\beta$ gets to $180^\circ$, the larger the change of ADCB will be, for a set displacement of C perpendicular to the ADC plane (red).

## 3 Interpolation of the ring opening

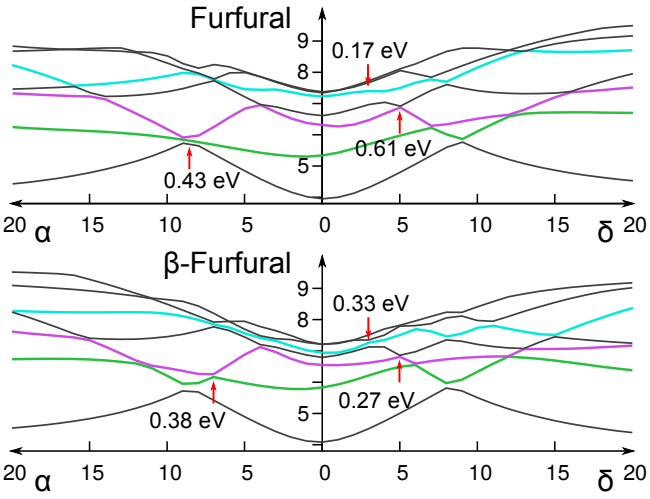


**Fig. S3** Interpolation between the FC structure (step 0) and the CoIn$_o$'s (step 20) of both possible sides ($\alpha$ and $\delta$) for furfural and $\beta$-furfural. The figure shows the the energies in eV of the excited states 1-7 compared to the groundstate minimum energy. At the FC point the $S_1$ (black line at 4 eV) is the $n_O\pi^*$ state, the $\pi\pi^*$ states are colored. From step 5 at the latest, one can easily follow one diabatic state, which crosses all the others and ends up in the $S_1$ shortly before step 10. This is the $\pi\sigma^*$ state. The lowest barriers of the interpolation of the opening process for all three $\pi\pi^*$ states are shown. They all are of comparable height; if exciatation to the $S_2$ (green) induces the opening reaction, excitation to the higher lying $\pi\pi^*$ states (magenta and cyan) most likely will do so, too.

## 4 Time resolved photo electron spectra

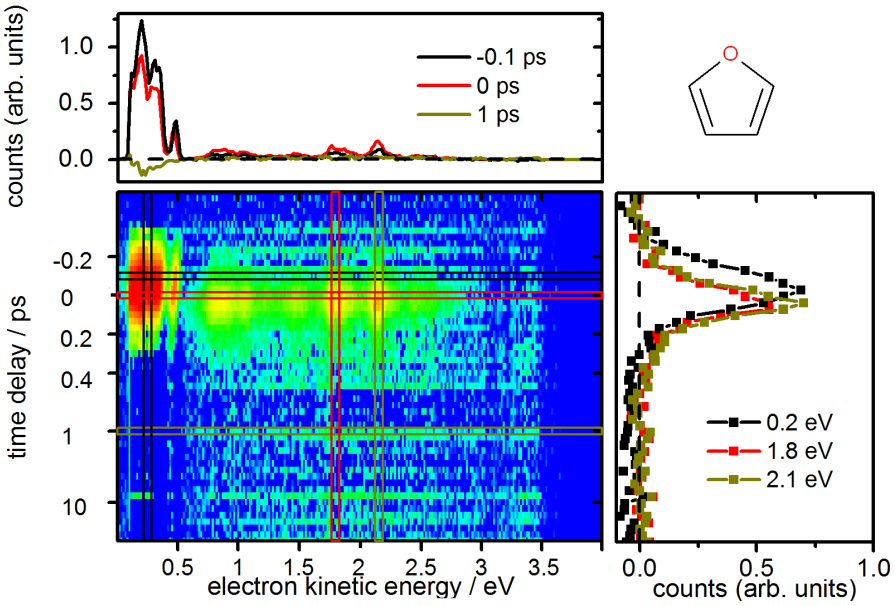


**Fig. S4** Time-resolved photoelectron spectra of furan upon excitation at 200 nm and ionization at 400 nm. The scaling factors for the cuts on the right are 4.5 (1.8 eV, red) and 4 (2 eV, ocher).

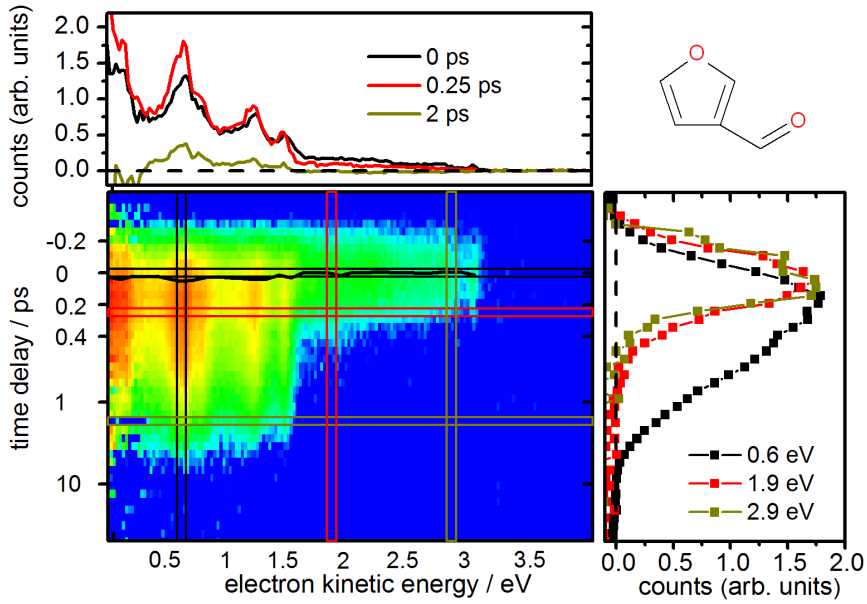


**Fig. S5** Time-resolved photoelectron spectrum of $\beta$-furfural upon excitation at 267 nm and ionization at 400 nm. The scaling factors for the cuts on the right are 9.5 (1.9 eV, red) and 26 (2.9 eV, ocher).

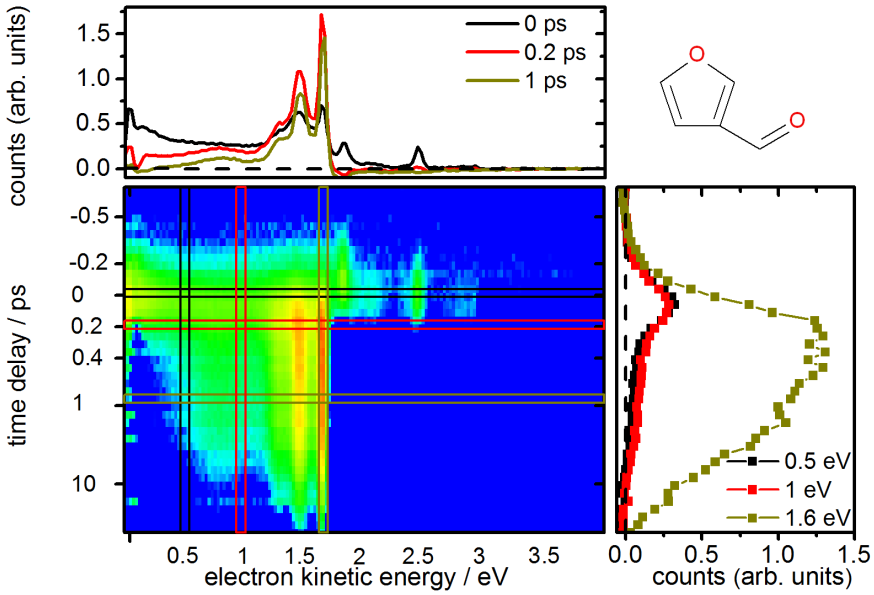


**Fig. S6** Time-resolved photoelectron spectrum of $\beta$-furfural upon excitation at 200 nm and ionization at 267 nm.

## 5 Semiclassical dynamics of furfural and $\beta$-furfural

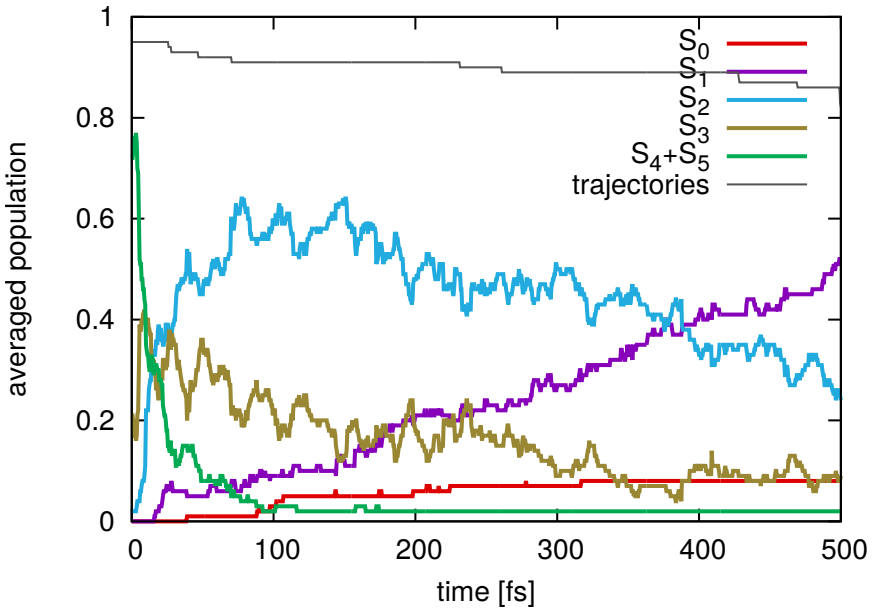


**Fig. S7** Excitated state population of the on-the-fly dynamics simulation of $\beta$-furfural averaged over 100 trajectories. Trajectories were started in the state most similar to $S_4$ of the FC, which is the state with the largest HOMO-LUMO contribution.

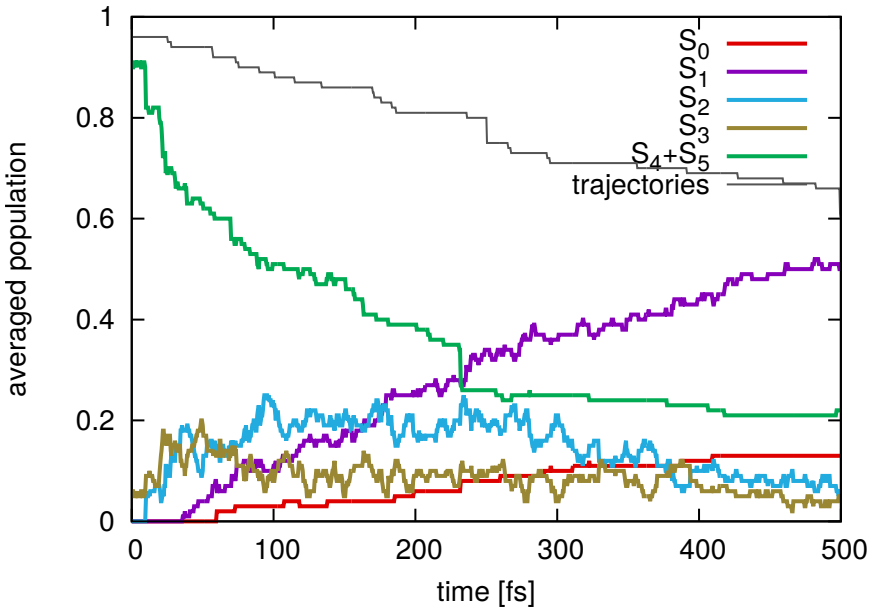


**Fig. S8** Excitated state population of the on-the-fly dynamics simulation of furfural averaged over 100 trajectories. Trajectories were started in the state most similar to $S_4$ of the FC, which is the state with the largest HOMO-LUMO contribution.

## 6 Detailed energy comparison for the (10,11) active space with the aug basis set

**Table S1** Comparing the energies of both CASSCF and RS2 calculations with the (10,9) active space for the basis sets 6-31G*, aug and 6-31+G*, the aug-basis does not behave anomalous. It is a subset of 6-31+G*, which had the diffuse s-functions removed, and thus yields absolute CASSCF excitation energies between 6-31G* and 6-31+G*, very close to the latter. The active spaces of both, aug and 6-31+G* can be increased, by adding two diffuse orbitals, which causes a significant decrease in the excitation energy of one of the $\pi\pi^*$ states, bringing it closer to the RS2 results. When using 6-31+G*, however, this (10,11) active space would not be stable and two additional 3s-like orbitals have to be included to form a (10,13) active space. Both orbitals introduce a new state to the calculation, which become the new $S_1$ and $S_2$. The $\pi\pi^*$ states are shifted to $S_3$ and $S_4$. All three, the (slightly) bigger basis, the bigger active space and the additional states, comparing aug (10,11) and 6-31+G* (10,13), cause an unnecessarily higher computation time.

| | (10,9) | | | (10,11) | | (10,13) |
|---|---|---|---|---|---|---|
| | 6-31G* | aug | 6-31+G* | aug | | 6-31+G* |
| CASSCF | | | excitation energies [eV] | | | CASSCF |
| $S_1$ | 6.796256 | 6.698674 | 6.698293 | 6.646177 | | exc.en. [eV] |
| $S_2$ | 8.004133 | 7.694074 | 7.694417 | 6.793356 | $S_1$ | 5.906673 |
| RS2 | | | | | $S_2$ | 6.320080 |
| $S_1$ | 6.720430 | 6.525020 | 6.518173 | 6.581834 | $S_3$ | 6.471927 |
| $S_2$ | 6.839735 | 6.585295 | 6.583562 | 6.628447 | $S_4$ | 6.650759 |
| CASSCF | | | absolute energies [H] | | | CASSCF |
| $S_1$ | -228.491897 | -228.498782 | -228.499271 | -228.531536 | | abs.en. [H] |
| $S_2$ | -228.447509 | -228.462201 | -228.462664 | -228.526127 | $S_1$ | -228.552970 |
| RS2 | | | | | $S_2$ | -228.537778 |
| $S_1$ | -229.055366 | -229.074985 | -229.077176 | -229.073263 | $S_3$ | -228.532198 |
| $S_2$ | -229.050982 | -229.072770 | -229.074773 | -229.071550 | $S_4$ | -228.525626 |

## 7 Electronic extent of selected orbitals in furan

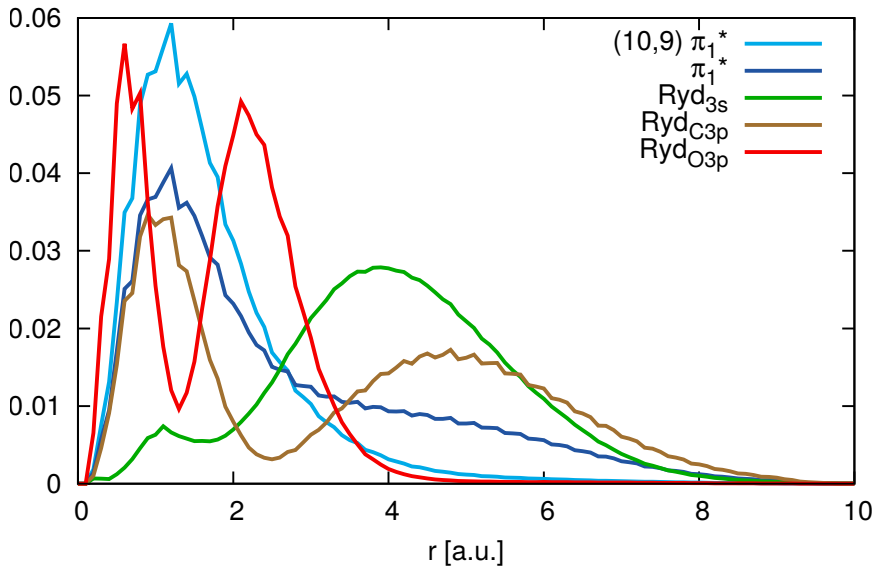


**Fig. S9** Square of the absolute value of the orbitals $\pi^*$, $Ryd_{3s}$, $Ryd_{C3p}$, and $Ryd_{O3p}$ as a function of $r$, where $r$ is the distance between the point considered, and the closest atom of furan. The integration was done numerically using cubefiles of the (10,9) 6-31+G* calculation for the (10,9) $\pi^*$, and the (10,13) 6-31+G* calculation for the other orbitals. The values shown are the integrated parts for every 0.1 a.u.. One can observe, that the increase of the active space affects the $\pi^*$ orbital, which mixes with $Ryd_{C3p}$ and $Ryd_{O3p}$, and incorporates some diffuse character.
The expectation values $\langle r^2 \rangle$ in $[a_0^2]$ for the orbitals are: (10,9) $\pi^*$: 3.82; $\pi^*$: 10.11; $Ryd_{3s}$: 18.68; $Ryd_{C3p}$: 16.87; $Ryd_{O3p}$: 4.03;

# 8 Optimized structures

| **furan** | | | **FC** |
|---|---|---|---|
| C | -1.099432 | -0.348557 | 0.000059 |
| C | -0.721080 | 0.963340 | -0.000009 |
| C | 0.721320 | 0.963155 | 0.000005 |
| C | 1.099336 | -0.348839 | 0.000017 |
| O | -0.000154 | -1.171749 | 0.000107 |
| H | -2.058524 | -0.851585 | -0.000021 |
| H | -1.379396 | 1.825509 | -0.000127 |
| H | 1.379857 | 1.825155 | 0.000007 |
| H | 2.058299 | -0.852113 | 0.000102 |

| **furan** | | | **CoIn**$_p$ |
|---|---|---|---|
| O | -0.103325 | 0.720065 | -1.376042 |
| C | -0.912929 | -0.032063 | -0.678576 |
| C | -0.593812 | -0.104519 | 0.765743 |
| C | 1.262193 | 0.163146 | -0.601778 |
| C | 0.734471 | 0.087930 | 0.813520 |
| H | -1.717642 | -0.526938 | -1.193275 |
| H | -1.321290 | -0.171420 | 1.552270 |
| H | 1.356540 | 0.203253 | 1.679011 |
| H | 1.304095 | -0.837293 | -1.026087 |

| **furan** | | | **CoIn**$_o$ |
|---|---|---|---|
| C | 0.025836 | -1.016724 | 1.205215 |
| C | -0.004221 | 0.313556 | 1.262174 |
| C | 0.006874 | 1.110572 | 0.045786 |
| C | 0.049989 | 0.449895 | -1.184541 |
| O | 0.079305 | -0.827734 | -1.266453 |
| H | 0.027242 | -1.829112 | 1.900533 |
| H | -0.037229 | 0.819814 | 2.214247 |
| H | -0.016948 | 2.182358 | 0.085406 |
| H | 0.059461 | 1.003467 | -2.111898 |

| **furfural** | | | **FC** |
|---|---|---|---|
| C | -0.273700 | -0.091372 | -0.000038 |
| C | 0.374379 | 1.120659 | -0.000036 |
| C | 1.775931 | 0.824936 | 0.000063 |
| C | 1.876715 | -0.542528 | 0.000029 |
| H | 2.716505 | -1.227054 | 0.000098 |
| H | 2.599341 | 1.531065 | 0.000020 |
| H | -0.106402 | 2.093049 | -0.000158 |
| C | -1.692524 | -0.459419 | 0.000034 |
| O | 0.640294 | -1.123830 | 0.000087 |
| H | -1.900011 | -1.549503 | 0.000132 |
| O | -2.593772 | 0.374854 | -0.000007 |

| **furfural** | | | **CoIn**$_p$ |
|---|---|---|---|
| C | -0.681742 | 0.877390 | 0.619839 |
| C | -0.001818 | 2.191249 | 0.821986 |
| C | 1.304177 | 1.902977 | 0.764931 |
| C | 1.500364 | 0.397344 | 0.702641 |
| H | 1.263360 | -0.006885 | 1.686383 |
| H | 2.122968 | 2.594887 | 0.733556 |
| H | -0.515166 | 3.131406 | 0.851594 |
| C | -2.075933 | 0.556002 | 0.973402 |
| O | -0.001912 | 0.014069 | -0.062597 |
| H | -2.401979 | -0.468006 | 0.823091 |
| O | -2.836461 | 1.430558 | 1.324899 |

| **furfural ($\delta$)** | | | **CoIn**$_o$ |
|---|---|---|---|
| C | -0.297797 | 0.002544 | -0.302135 |
| C | 0.926658 | 0.000202 | 0.372438 |
| C | 0.914385 | -0.003964 | 1.824124 |
| C | -0.236061 | -0.005521 | 2.496414 |
| H | -0.545937 | -0.008327 | 3.519749 |
| H | 1.855828 | -0.005757 | 2.350256 |
| H | 1.842841 | 0.001498 | -0.182589 |
| C | -0.376768 | 0.006826 | -1.795352 |
| O | -1.418579 | 0.001046 | 0.326721 |
| H | -1.382800 | 0.008349 | -2.207366 |
| O | 0.598889 | 0.008460 | -2.503569 |

| **furfural ($\alpha$)** | | | **CoIn**$_o$ |
|---|---|---|---|
| C | -0.152978 | -0.060642 | -0.544076 |
| C | 1.004366 | 0.023807 | 0.126888 |
| C | 1.035623 | -0.070560 | 1.564158 |
| C | -0.179860 | -0.254005 | 2.250119 |
| H | -0.196533 | -0.329256 | 3.327827 |
| H | 1.959105 | -0.003629 | 2.105332 |
| H | 1.923772 | 0.164324 | -0.418306 |
| C | -0.568310 | -0.012047 | -1.941920 |
| O | -1.290992 | -0.337201 | 1.637144 |
| H | -1.630071 | -0.118038 | -2.138889 |
| O | 0.219875 | 0.138498 | -2.849320 |

| **furfural** | | | **CoIn**$_n$ |
|---|---|---|---|
| C | -0.347423 | 0.154204 | -0.059493 |
| C | 0.461083 | 1.310101 | 0.246755 |
| C | 1.798185 | 0.906798 | 0.150380 |
| C | 1.790195 | -0.432717 | -0.156198 |
| H | 2.565121 | -1.140245 | -0.348358 |
| H | 2.672261 | 1.511739 | 0.271872 |
| H | 0.062322 | 2.281767 | 0.438472 |
| C | -1.747089 | 0.100408 | -0.154951 |
| O | 0.493412 | -0.934589 | -0.231448 |
| H | -2.454794 | -0.685458 | 0.007688 |
| O | -1.451081 | 0.627489 | -1.369414 |

| $\beta$-furfural | | | FC |
|---|---|---|---|
| C | -1.841042 | -0.092570 | 0.003702 |
| C | -0.468347 | -0.092455 | 0.000043 |
| C | -0.067117 | 1.296084 | -0.001976 |
| C | -1.221859 | 2.017267 | 0.000571 |
| O | -2.322925 | 1.181811 | 0.004042 |
| H | -2.585893 | -0.880607 | 0.006052 |
| H | 0.950166 | 1.670844 | -0.005267 |
| H | -1.447755 | 3.076272 | 0.000370 |
| C | 0.410661 | -1.269667 | -0.001952 |
| O | 1.636417 | -1.195460 | -0.005553 |
| H | -0.098649 | -2.258117 | 0.000097 |

| $\beta$-furfural ($\delta$) | | | $\mathbf{CoIn}_p$ |
|---|---|---|---|
| C | -1.854009 | -0.022782 | -0.012777 |
| C | -0.364492 | -0.100274 | -0.028582 |
| C | -0.009933 | 1.200532 | -0.035203 |
| C | -1.238805 | 2.046686 | 0.032086 |
| O | -2.328694 | 0.965825 | 0.692883 |
| H | -2.543403 | -0.655649 | -0.545486 |
| H | 0.982176 | 1.607191 | -0.036788 |
| H | -1.684831 | 2.210649 | -0.942210 |
| C | 0.460343 | -1.312054 | 0.030336 |
| O | 1.668626 | -1.289924 | 0.045763 |
| H | -0.071449 | -2.263827 | 0.045322 |

| $\beta$-furfural ($\alpha$) | | | $\mathbf{CoIn}_p$ |
|---|---|---|---|
| C | -1.907214 | -0.159871 | -0.113015 |
| C | -0.387324 | -0.104924 | -0.043772 |
| C | -0.025347 | 1.196825 | -0.102481 |
| C | -1.284147 | 1.935026 | 0.054057 |
| O | -2.242039 | 1.278320 | 0.645647 |
| H | -2.193975 | 0.136556 | -1.119740 |
| H | 0.949402 | 1.643211 | -0.143385 |
| H | -1.480029 | 2.949530 | -0.245691 |
| C | 0.487691 | -1.281664 | 0.061731 |
| O | 1.693159 | -1.212558 | -0.024172 |
| H | -0.006525 | -2.234677 | 0.231880 |

| $\beta$-furfural($\delta$) | | | $\mathbf{CoIn}_o$ |
|---|---|---|---|
| C | 0.000006 | -1.009590 | 1.196458 |
| C | 0.000001 | 0.318967 | 1.253507 |
| C | -0.000000 | 1.114980 | 0.034011 |
| C | 0.000003 | 0.434895 | -1.204393 |
| O | 0.000007 | -0.831428 | -1.280659 |
| H | 0.000008 | -1.825158 | 1.887778 |
| H | -0.000001 | 0.839190 | 2.196310 |
| C | -0.000005 | 2.572395 | 0.072088 |
| H | 0.000001 | 0.989882 | -2.132769 |
| H | -0.000006 | 3.087738 | -0.887261 |
| O | -0.000008 | 3.213325 | 1.103338 |

| $\beta$-furfural ($\alpha$) | | | $\mathbf{CoIn}_o$ |
|---|---|---|---|
| C | 0.000005 | -1.008315 | 1.185100 |
| C | 0.000001 | 0.326943 | 1.254890 |
| C | -0.000000 | 1.118782 | 0.028561 |
| C | 0.000003 | 0.440706 | -1.189210 |
| O | 0.000007 | -0.842113 | -1.249009 |
| H | 0.000007 | -1.818027 | 1.884874 |
| C | -0.000003 | 1.017974 | 2.569695 |
| H | -0.000004 | 2.188766 | 0.073507 |
| H | 0.000002 | 0.975205 | -2.126680 |
| H | -0.000002 | 0.379360 | 3.451237 |
| O | -0.000007 | 2.219115 | 2.683271 |

| $\beta$-furfural | | | $\mathbf{CoIn}_n$ |
|---|---|---|---|
| C | -2.084951 | -0.016517 | -0.058198 |
| C | -0.720796 | -0.334855 | 0.180877 |
| C | -0.055976 | 0.966803 | 0.284230 |
| C | -0.999565 | 1.887327 | 0.048213 |
| O | -2.263639 | 1.350801 | -0.153348 |
| H | -2.944843 | -0.632621 | -0.179546 |
| H | 0.982492 | 1.144199 | 0.464495 |
| H | -0.961278 | 2.953885 | -0.004177 |
| C | -0.364605 | -1.688904 | 0.306387 |
| O | -0.411197 | -1.547569 | -1.076579 |
| H | 0.380263 | -2.228925 | 0.845893 |