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

Electronic Supplementary Information for:

Ultrafast dynamics of UV-excited *trans*- and *cis*-ferulic acid in aqueous solutions

Shuangqing Wang,[1] Sebastian Schatz,[1] Mayra C. Stuhldreier,[1, 2] Hendrik Böhnke,[1] Joss Wiese,[1, 3] Carsten Schröder,[1] Tim Raeker,[1] Bernd Hartke,[1] Julia K. Keppler,[4] Karin Schwarz,[4] Falk Renth,[1, a)] and Friedrich Temps[1, a)]

1) *Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel,*
Olshausenstr. 40, 24098 Kiel, Germany

2) *Present address: TNG Technology Consulting GmbH, Betastraße 13a,*
85774 Unterföhring, Germany

3) *Present address: Center for Free-Electron Laser Science (CFEL),*
Deutsches Elektronen-Synchrotron DESY, 22607 Hamburg,
Germany

4) *Institut für Humanernährung und Lebensmittelkunde, Christian-*
Albrechts-Universität zu Kiel, Heinrich-Hecht-Platz 10, 24118 Kiel,
Germany

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a) Authors to whom correspondence should be addressed;renth@phc.uni-kiel.de, temps@phc.uni-kiel.de

Calculated molecular orbitals of the *trans*- and *cis*-ferulic acid isomers

The DFT calculations were carried out using the Turbomole 7.0 program package[1], employing the Conductor-like Screening Model (COSMO)[2–4] to take into account solvation effects (see Sec. 2.3 of the main article). The relevant molecular orbitals (MOs) for the electronic transitions $S_0 \rightarrow S_n$ up to $n = 4$ of the bare neutral, anionic and di-anionic forms of *trans*- and *cis*-ferulic acid (FA) are displayed in Figures S1 and S2.

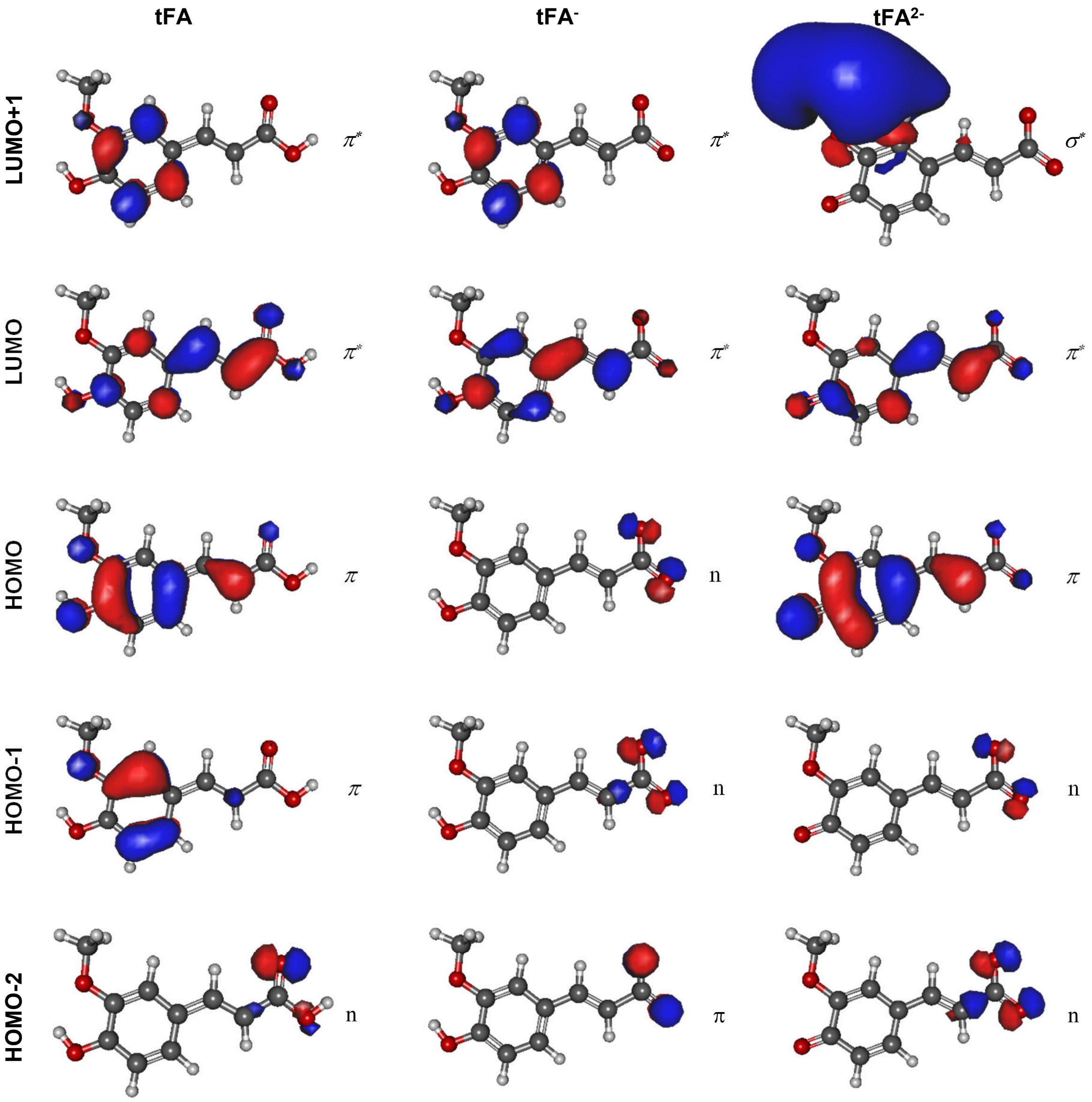

Fig. S1. Relevant molecular orbitals and their deduced characters of *trans*-FA in its neutral, anionic and di-anionic forms (tFA, tFA^{-} and tFA^{2-}) *in vacuo*.

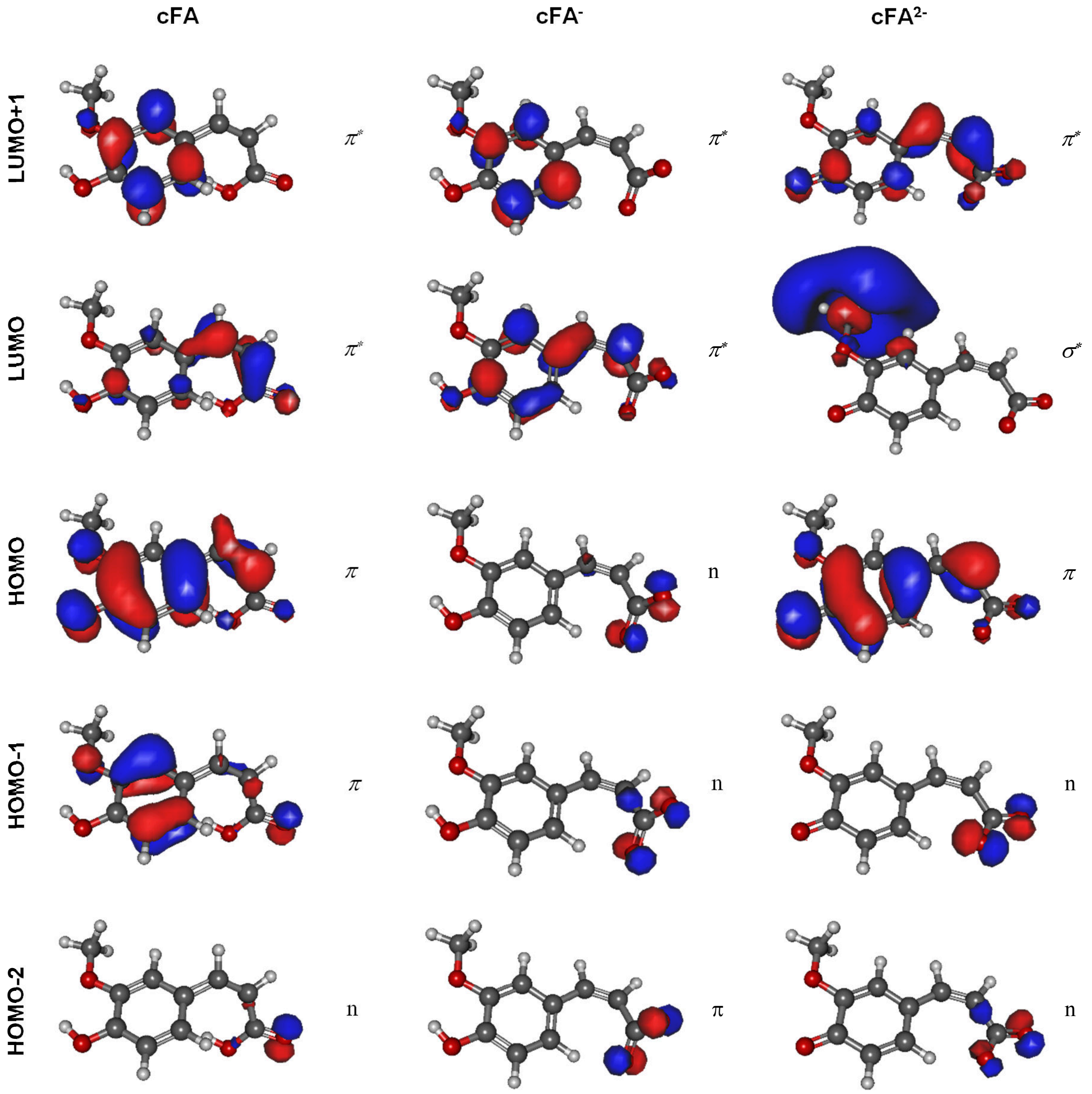

Fig. S2. Relevant molecular orbitals and their deduced characters of *cis*-FA in its neutral, anionic and di-anionic forms (cFA, cFA$^-$ and cFA^{2-}) *in vacuo*.

The characters of the orbitals judged from visual inspection are indicated to their right. Mutual comparison of the *trans* and *cis* isomers reveals that the neutral tFA and cFA forms, and likewise the anionic tFA$^-$ and cFA$^-$ forms share the same sequence of orbitals. For the dianionic forms, the LUMO and LUMO+1 orbitals are interchanged. The unoccupied orbitals have π^* character and show electron density at the benzene ring (LUMO+1) and at the C=C double bond (LUMO). Only for the dianionic forms, a σ^*-like orbital replaces the π^* LUMO+1 orbital (tFA^{2-}) or the π^* LUMO orbital (cFA^{2-}). Indications for optically dark $\pi\sigma^*$ states have also been found in recent CASSCF/CASPT2 calculations for tFA and cFA, and they do play an important role in the photophysics of phenolic molecules.[5–8] However, we refrain from drawing any conclusions, considering that the calculations with inclusion of solvation effects do not show such states, and being cautious when interpreting DFT results regarding excited-state pathways (see further below). The occupied orbitals have either π- or n-character, and the transitions from the highest-lying π-orbital to the π^* LUMO (LUMO+1 for cFA^{2-}) are optically allowed $S_0 \rightarrow {}^1\pi\pi^*$ transitions in all cases.

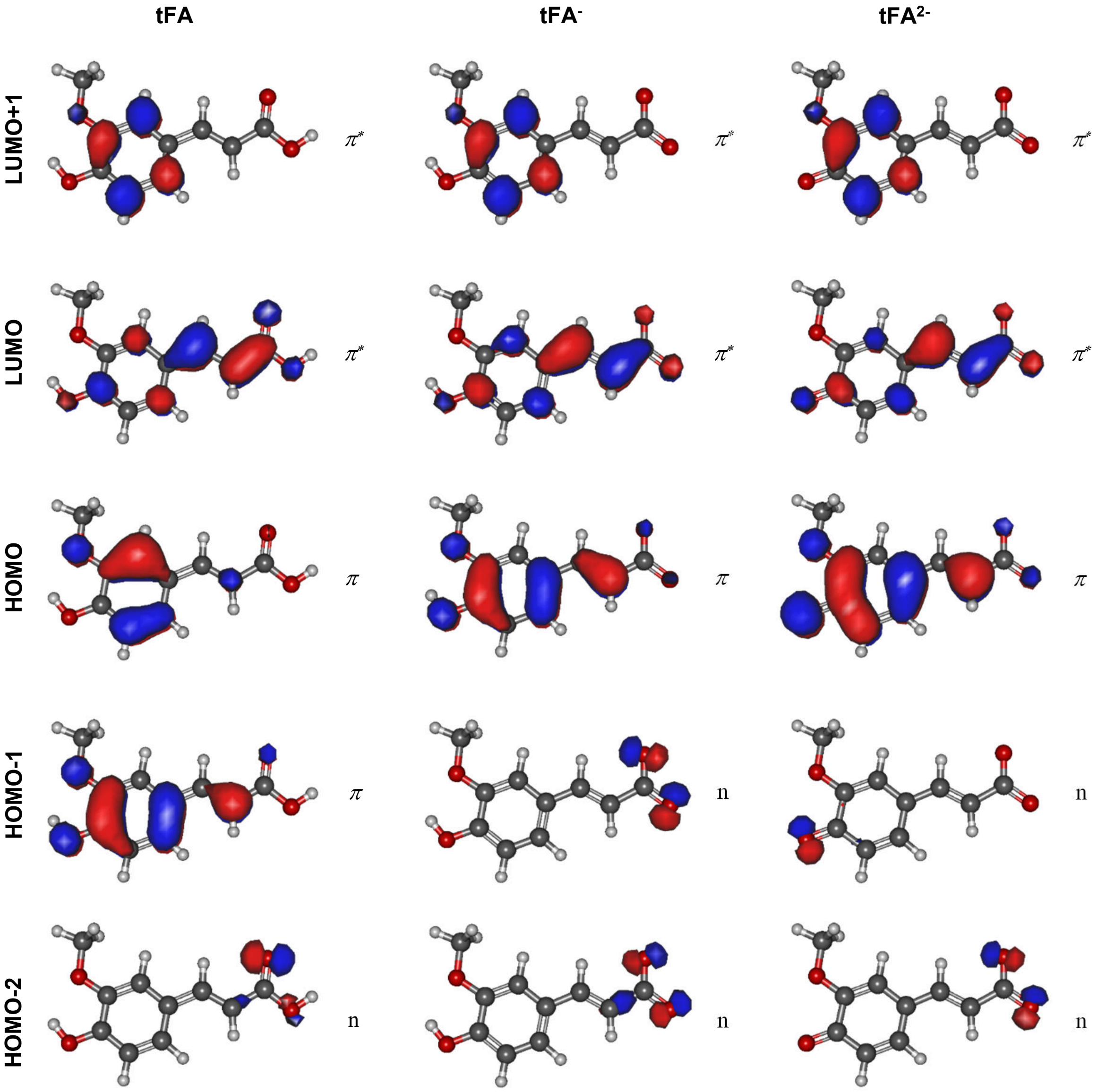

Fig. S3. Relevant molecular orbitals and their deduced characters for the neutral, anionic and di-anionic forms of *trans*-FA with solvation effects taken into account.

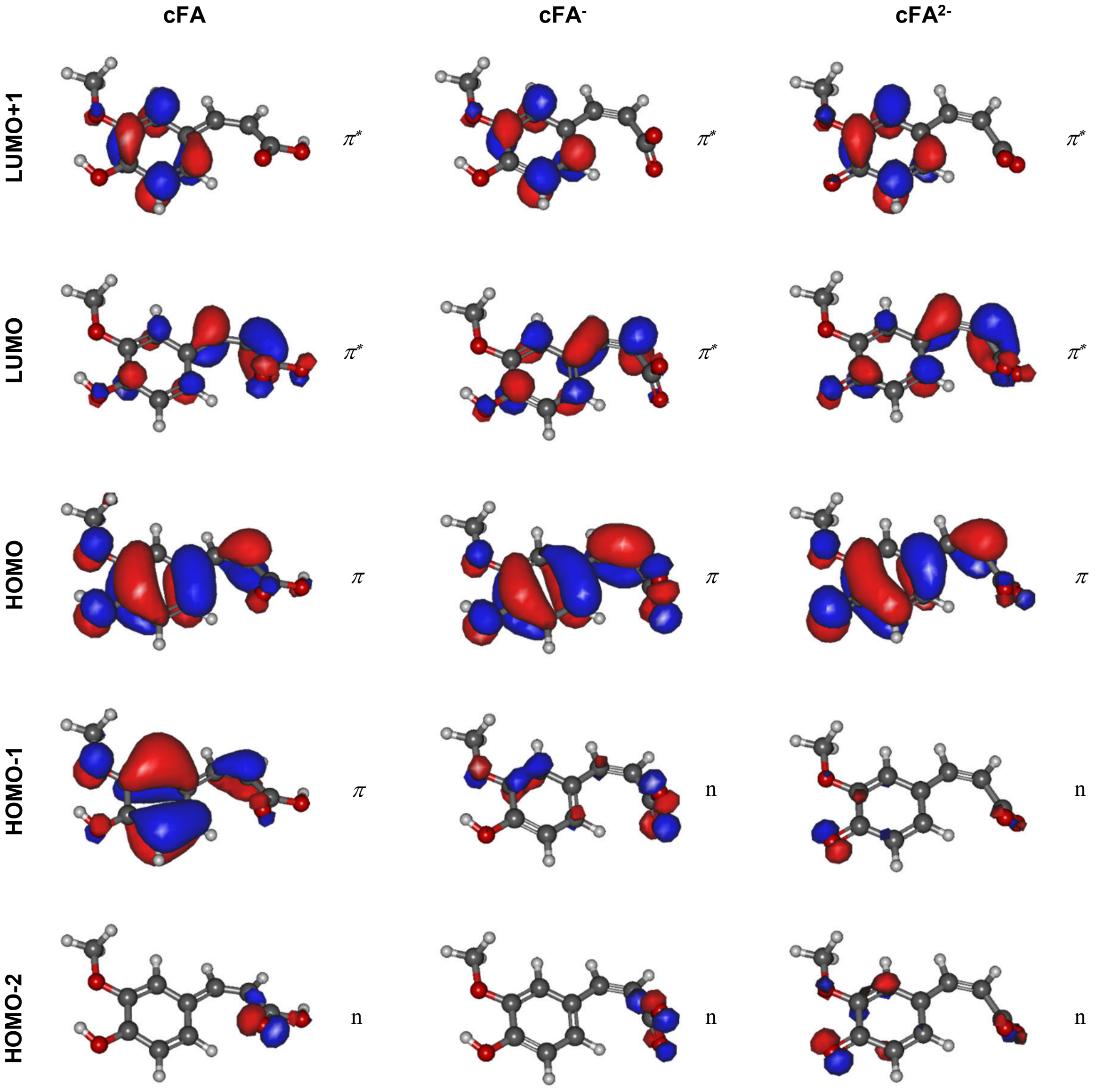

Fig. S4. Relevant molecular orbitals and their deduced characters for the neutral, anionic and di-anionic forms of *cis*-FA with solvation effects taken into account.

Figures S3 and S4 show the relevant MOs for the electronic transitions $S_0 \rightarrow S_n$ up to $n = 4$ for the different forms of *trans*- and *cis*-FA obtained with inclusion of solvation effects. As can be seen, the respective *trans*- and *cis*-forms have the same sequences of orbital characters. The unoccupied orbitals are all of π^* character, located either at the benzene ring (LUMO+1) or the C=C double bond (LUMO), the HOMO is always of π character. The neutral forms tFA and cFA have a second, lower-lying π orbital as HOMO-1, which is replaced by a n orbital for the anionic and dianionic forms. The HOMO-2 orbitals are n

orbitals located at the oxygen atoms of the acid group, except for cFA^{2-}, where the phenolic O-atom is also involved. In the latter case, the visual difference between the HOMO-1 and HOMO-2 orbitals is rather small, which is also reflected in the strong mixing character for the excitations involving these orbitals.

As stated in the paper, vertical excitation populates the $1\,^1\pi\pi^*$ state via an optically allowed $S_0 \rightarrow {}^1\pi\pi^*$ transition in all cases. Judged from the orbitals in Figures S3 and S4, these HOMO-LUMO transitions move an electron from a bonding C=C π orbital to an anti-bonding π^* orbital. This could be interpreted in favour of a photo-induced *cis* $\rightleftarrows$ *trans* isomerisation coordinate, conforming to the standard expectation at photo-excited double bonds.[9] However, such a conclusion should be drawn only with great caution, since molecular orbitals are just convenient computational constructs (which could be transformed via arbitrary linear transforms) and do not correspond to observables. Furthermore, when multi-configuration interaction is taken into account, concepts like HOMO and LUMO become ill-defined. Second, for an investigation of the de-excitation pathways, even a scan of the C=C dihedral angle would provide little evidence on how much this particular mechanism contributes; only unbiased, full-dimensional direct-dynamics simulations could provide these answers. For (TD)DFT or any other type of single-reference electronic structure method, such calculations are hardly adequate because of the expected strong coupling between the participating electronic states, and the likely involvement of conical intersections (CIs), which cannot be treated correctly by these methods.[10]. It should be noted that our calculations could be interpreted in favour the $^1n\pi^*$ states playing a role in the FA photochemistry, in line with previous calculations *in vacuo* on these molecules.[8,11] However, our calculations were done only at the optimized ground-state geometries, where indeed a good agreement with earlier CASSCF/CASPT2 results[8] was found (see paper). But given the approximations inherent in our method (RPA-DFT) and other standard TDDFT variants, this does not imply good results in other regions of the potential energy surfaces (PES); in fact, qualitative failures at conical intersections are to be expected. Therefore, our results provide a hint at a possible involvement of the $^1n\pi^*$ states, but their exact role and importance cannot be deduced.

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