Supplementary Information:

Resonance Enhanced MultiPhoton Ionization studies of di-ortho-methoxy methylcinnamate, a cinnamate-based UV-B filter

Ivan Romanov[1], Michael Hymas[2], Jack Dalton[2], Vasilios G. Stavros[2] and Wybren Jan Buma[1,3*],

[1] *Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands*

[2] *School of Chemistry, University of Birmingham, Edgbaston, B15 2TT, United Kingdom*

[3] *Institute for Molecules and Materials, FELIX Laboratory, Radboud University, 6525 ED Nijmegen, The Netherlands*

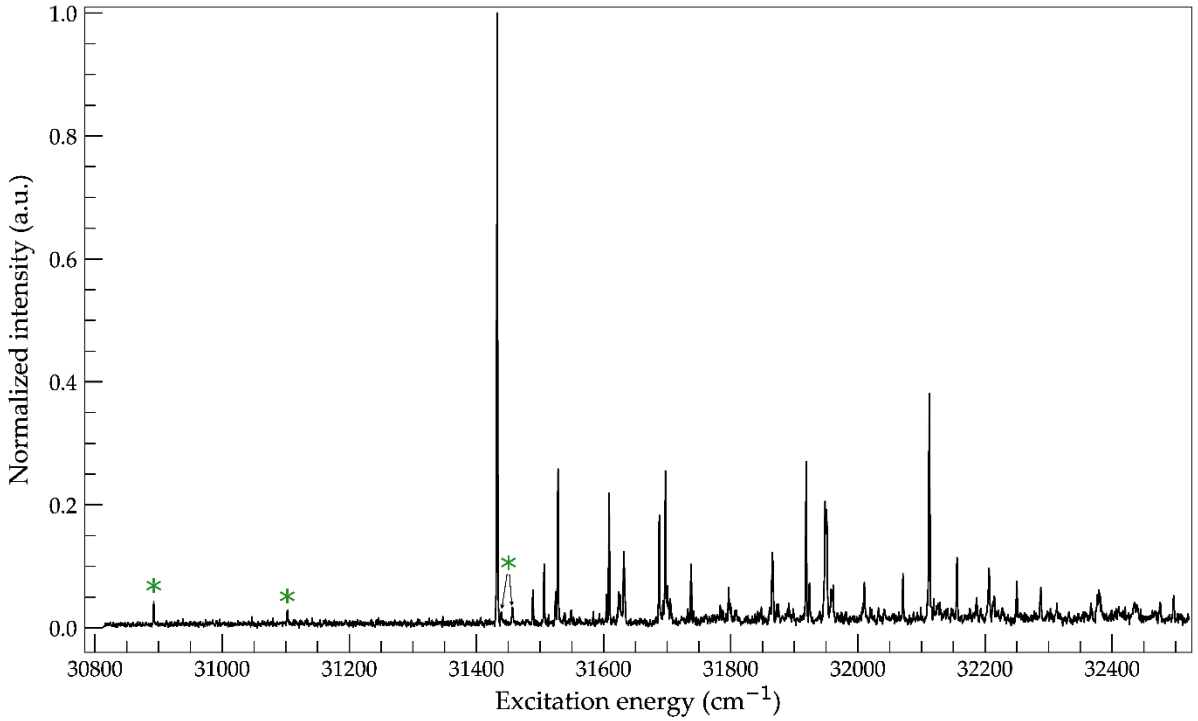

Figure S1. Extended jet-cooled excitation spectrum of di-ortho-methoxy methylcinnamate (**1**) recorded by two-colour (1+1') R2PI spectroscopy. Bands indicated with an ∗ are assigned to resonances of **1**-H_2O clusters.

Table S1. Composition wavefunctions V'($\pi\pi^*$) and V($\pi\pi^*$) states of s-*cis* and s-*trans* conformations of di-*ortho*-methoxy cinnamate at S_0 equilibrium geometry (vertical) and at the equilibrium geometry of the respective electronically excited state (adiabatic). HOMO and LUMO are abbreviated as H and L.

	Vertical s-*cis*	Adiabatic s-*cis*[a]	Vertical s-*trans*	Adiabatic s-*trans*[a]
V'($\pi\pi^*$)	H-1→ L 0.62 H → L -0.28 H → L+1 -0.17	H-1→ L 0.62 H → L -0.30 H → L+1 -0.13	H-1→ L 0.66 H → L -0.18 H → L+1 -0.18	H-1→ L 0.65 H → L -0.23 H → L+1 -0.13
V($\pi\pi^*$)	H-1→ L 0.27 H → L 0.64		H-1→ L 0.18 H → L 0.68	

[a] Geometry optimization of the V($\pi\pi^*$) state does not lead to a stable minimum.