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

Supporting Information

Elucidating the photoprotective properties of natural UV screening agents: ZEKE-PFI spectroscopy of methyl sinapate

Jiayun Fan[a], Laura Finazzi[a] and Wybren Jan Buma[*ab]

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

[b] Radboud University, Institute for Molecules and Materials, FELIX Laboratory, Toernooiveld 7c, 6525 ED Nijmegen, The Netherlands.

[*] Email: w.j.buma@uva.nl

Table S1 Assignment of higher-intensity bands observed in ZEKE-PFI spectrum of D_0 after excitation from vibrationless level of S_1 of the *syn/cis* conformer of methyl sinapate for bands up to vibrational excess energies of ~500 cm^{-1}.

Frequency (cm^{-1})[a,d]	Intensity (%)[b]	Assignment[c]
0.0	100	
59.9	164	56^1
120.5	132	56^2
162.8	22	55^1
180.1	72	56^3
223.0	34	$55^1 56^1$
235.1	33	53^1
240.3	37	56^4
270.3	21	52^1
276.4	27	-
284.3	40	$55^1 56^2$
294.3	27	$53^1 56^1$
298.6	19	56^5
321.7	14	51^1
330.5	38	$52^1 56^1$
336.2	41	$276.4+56^1$
344.5	31	$55^1 56^3$
354.5	20	$53^1 56^2$
380.5	15	$51^1 56^1$
390.5	35	$52^1 56^2$
395.3	33	$276.4+56^2$
404.5	22	$55^1 56^4$
411.7	16	$53^1 56^3$
439.7	19	$51^1 56^2$
455.1	22	$52^1 56^3$
473.2	15	$53^1 56^4$
432.4	7	$52^1 55^1$
500.1	19	$51^1 56^3$

[a] Frequency with respect to D_0 adiabatic ionization energy from vibrationless level of S_0 (60291.1 cm^{-1}).

[b] Intensity with respect to intensity of $D_0 \leftarrow S_1$ 0-0 band. Starting from energies above ~200 cm^{-1} bands are superimposed on a background signal that masks true band intensities.

[c] Standard labelling vibrational modes: a'(1-56), a''(57-87) with decreasing frequencies.

[d] For vibrational excess energies higher than ~500 cm^{-1} the ZEKE-PFI spectrum still shows quite a number of bands with minor intensities but these cannot be assigned unambiguously.

Table S2 Assignment of higher-intensity bands observed in ZEKE-PFI spectrum of D_0 after excitation from vibrationless level of S_1 of the *anti/cis* conformer of methyl sinapate for bands up to vibrational excess energies of ~400 cm^{-1}.

Frequency (cm^{-1})[a,d]	Intensity (%)[b]	Assignment[c]
0.0	100	
60.2	69	56^1
119.8	25	56^2
163.3	5	55^1
171.9	3	54^1
179.2	4	56^3
223.7	4	$55^1 56^1$
230.7	4	$54^1 56^1$
267.9	5	52^1
277.5	2	-
281.4	1	$55^1 56^2$
291.8	1	$54^1 56^2$
319.7	1	51^1
326.6	2	$52^1 56^1$
336.2	1	$277.5+56^1$
353.7	1	50^1
380.3	1	$51^1 56^1$
386.9	1	$52^1 56^2$

[a] Frequency with respect to D_0 adiabatic ionization energy from vibrationless level of S_0 (60366.9 cm^{-1}).
[b] Intensity with respect to intensity of $D_0 \leftarrow S_1$ 0-0 band.
[c] Standard labelling vibrational modes: a'(1-56), a"(57-87) with decreasing frequencies.
[d] For vibrational excess energies higher than ~400 cm^{-1} the ZEKE-PFI spectrum still shows quite a number of bands with minor intensities but these cannot be assigned unambiguously.

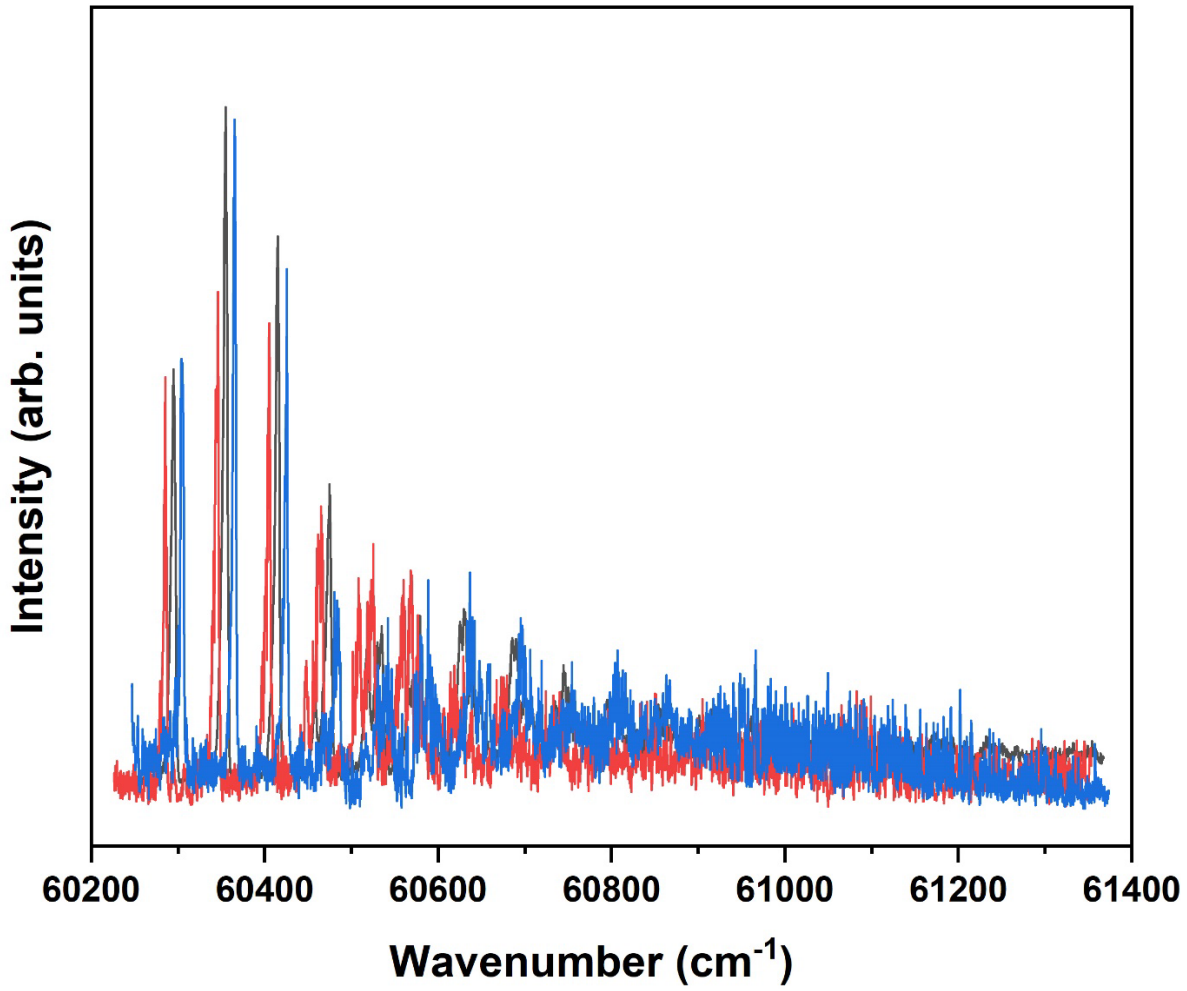

Figure S1 Time-dependent ZEKE spectra obtained for excitation at the $S_1 \leftarrow S_0$ origin transition (31059.8 cm-1) of the *syn*/*cis* conformer of MS for a delay between excitation and ionization laser of -10 ns (red), 0 ns (black), and +10 ns (blue). For clarity traces have been displaced horizontally with respect to each other. Figure S1 is the full-range version of Figure 8 in the main article.