Supporting Online Material

Excited-State Dynamics of Isolated and Microsolvated Cinnamate-Based UV-B Sunscreens

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Contents

1. Experimental details.

In the molecular beam experiment the sample was heated to 130 °C and expanded with Ne at a pressure of 3 bars via a 0.5 mm nozzle into a vacuum to create a supersonic expansion. The two-color Resonance Enhanced MultiPhoton Ionization (REMPI) excitation spectrum was measured over the range of 32000-35000 cm^{-1} using a frequency-doubled Nd:YAG (Spectra Physics Lab 190) pumped dye laser (Sirah Precision Scan) operating at 30 Hz. The excitation pulse energy was typically 1-2 mJ. The laser beams were not focused to avoid saturation although partial saturation can still be observed in the REMPI and UV-UV depletion spectra. The counter-propagating ionization beam was produced by an ArF excimer (Neweks PSX-501) laser (193 nm) and was introduced simultaneously with the excitation pulses.

For the investigation of conformer-specific spectra UV-UV depletion experiments were performed. The additional pump laser pulses were introduced 160-200 ns before the excitation-ionization beam sequence and were generated by a second dye laser (Sirah Cobra-Stretch) pumped by a second frequency-doubled Nd:YAG laser (Spectra Physics Lab 190). The frequency of the excitation laser was fixed at bands that were associated exclusively with a single conformation (32328.2 and 32667.4 cm^{-1} for the s-*cis* and s-*trans* conformer of MMC respectively). The same method was used for EHMC for which the excitation laser was fixed at 32258 and 32562 cm^{-1} for the s-*cis* group and s-*trans* group of conformations respectively. While scanning the wavelength of the pump beam and recording the signal produced by the probe, we observe a depletion of the probe signal as a result of the depopulation of the ground state each time the pump laser is in resonance with a transition of the selected conformer. The pulse energies and focusing conditions for excitation and ionization beams in these experiments were identical to those used in the REMPI experiments. In case of the UV-depletion experiments the pulse energy of the pump beam was 1.5 mJ.

In all experiments (REMPI as well as UV-UV depletion) the ions created during the multiphoton ionization process were accelerated into a time of flight (TOF) mass spectrometer equipped with a reflectron (R.M. Jordan Co.) and detected using a multichannel plate detector. Mass-resolved excitation and depletion spectra were recorded by monitoring the ion signal at the methyl 4-methoxycinnamate (MMC) mass channel (192 a.m.u.), MMC-water cluster mass channel (210 a.m.u), and 2-ethylhexyl 4-methoxycinnmate (EHMC) mass channel (290 a.m.u.).

2. Theoretical details

Using the spin-component scaled version of the approximate coupled-cluster singles-and-doubles model (SCS-CC2)[1,2], ground state geometry optimizations followed by calculation of vertical energies of the electronic excited states of interest were performed using the resolution-of-the-identity approximation (RICC2) module as implemented in the TURBOMOLE package[3]. For the vertical energies calculations, the Dunning's correlation consistent polarized double zeta basis set augmented with the standard auxiliary basis sets (aug-cc-pVDZ)[4,5] was employed.

Franck-Condon intensities for vibronic spectra of MMC conformers were calculated in the harmonic approximation and taking into account Duschinsky mixing. To this purpose ground state geometry optimizations and normal mode calculations were performed with Density Functional Theory (DFT) using the B3LYP hybrid functional and the cc-pVDZ basis set[4]. Time Dependent Density Functional Theory (TDDFT) using the same functional and basis set was employed to perform excited state geometry optimizations and normal mode calculations. All calculations were performed with the Gaussian09 suite of programs[6] in which calculation of vibrational integrals has been implemented to predict the vibrationally resolved absorption spectrum by utilizing the prescreening technique to choose *a priori* the most intense transitions. For the comparison with experimental spectra a scaling factor of 0.970 was used for the predicted frequencies. As will be shown below, we find that the vibrational activity observed in the conformation-specific experimental spectra of MMC can be reproduced satisfactorily using the equilibrium geometry and force field of the V'($\pi\pi^*$) state for all conformations, thereby confirming the assignment of the s-*cis* and s-*trans* conformers.

3. Vertical excitation energies MMC.

Table S1 provides the vertical excitation energies of the s-*cis* conformer of MMC as obtained from calculations at the SCS-CC2/aug-cc-pVDZ level. Similar to pCA[7] and OMpCA[8–10] we find that at the equilibrium geometry of the ground state S_1 is associated with the V'($\pi\pi$*) state, S_2 with the V($\pi\pi$*) state, and S_3 with the nπ* state.

State	Excitation energy (eV)	
V'($\pi\pi$*)	4.38903	(0.334)
V($\pi\pi$*)	4.58649	(0.564)
nπ*	5.05895	(6×10^{-5})

Table S1. Vertical excitation energies (eV) and oscillator strengths of the transitions to the lower electronically excited states of the s-*cis* conformer of MMC calculated at the SCS-CC2/aug-cc-pVDZ level.

4. Franck-Condon simulations of V'($\pi\pi^*$) $\leftarrow$ S$_0$ excitation spectra of s-*cis* and s-*trans* MMC

Figure S1a displays the (1+1') RE2PI excitation spectrum of MMC. For the parent compound OM*p*CA it has been shown that under molecular beam conditions the molecule can adopt four different conformations associated with the orientation of the OH group (*syn* or *anti*) and the orientation of the ester with respect to the propenyl C$_8$−C$_9$ single bond (s-*cis* or s-*trans*). When UV-UV depletion spectroscopy is applied to MMC only two species can be distinguished (Figure S1b and S1d). In view of the energy difference between the two origin transitions, we conclude that these two conformations are the ones associated with s-*cis* and s-*trans*, and that a potential conformational heterogeneity associated with the orientation of the methoxy group cannot be resolved. Figures S1c and S1e display predictions of the vibrational activity in the excitation spectrum of the s-*cis* and s-*trans* conformers. In these spectra the 0-0 transition has been cut off to allow for a better comparison of the experimentally observed and theoretically predicted vibrational activity. Bearing in mind that the RE2PI and UV-UV depletion spectra have been obtained under excitation conditions for which partial saturation of a number of transitions occurs[11], we find that the predicted spectra agree well with the experimental spectra as depicted in Figure S1b and S1d, respectively. We therefore conclude that the excitation spectrum with its origin at 32328.2 cm^{-1} should be assigned to the s-*cis* conformer, and the excitation spectrum with its origin at 32667.4 cm^{-1} to the s-*trans* conformer.
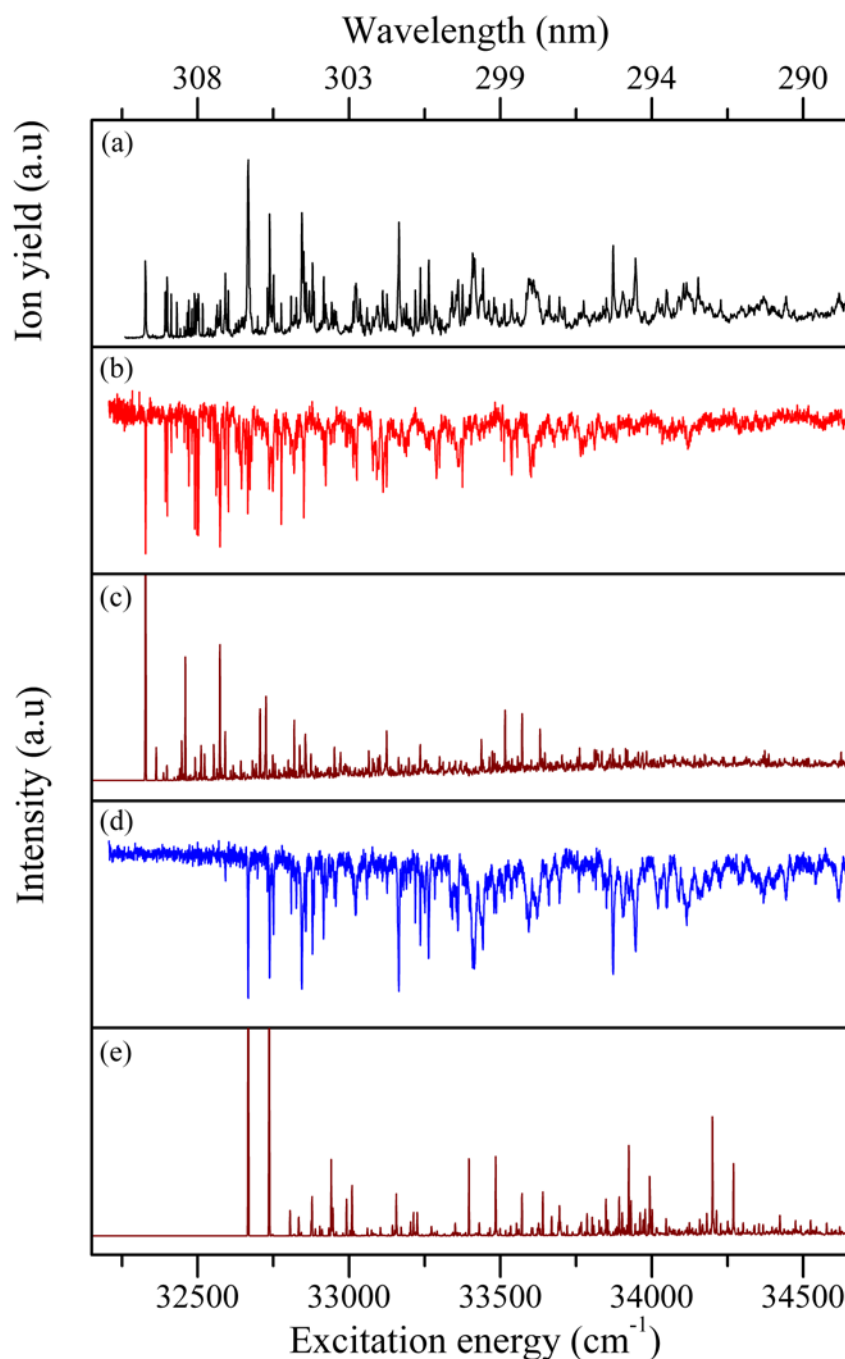
Figure S1. Comparison of UV-UV depletion spectra of MMC with Franck-Condon simulations of the s-*cis* and s-*trans* conformers. (a) (1+1') RE2PI excitation spectrum, (b) UV-UV depletion spectrum obtained for a probe energy of 32328.2 cm^{-1}, (c) Frank-Condon simulation of the V'($\pi\pi$*) excitation spectrum of the s-*cis* conformer, (d) UV-UV depletion spectrum obtained for a probe energy of 32667.4 cm^{-1}, (c) Frank-Condon simulation of the V'($\pi\pi$*) excitation spectrum of the s-*trans* conformer.

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