Electronic Supplementary Information

Analysis of the Time-Resolved FTIR Spectra of Alkyl Phenylglyoxylates: Implications on the Photoinitiation Step in Acrylate Polymerization.

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I. Synthetic procedures.

Materials and Solvents.

The following chemicals were commercially available and were used as received: Methyl phenylglyoxylate (Aldrich), ethyl phenylglyoxylate (Aldrich), benzoylformic acid (Aldrich), *N,N'*–dicyclohexylcarbodiimide (DCC) (Acros), 2,2,2-trichloroethanol (Acros), 2,2,2-trifluoroethanol (Acros). Dichloromethane was distilled from calcium hydride prior to use.

General Methods:

Melting points were determined with a Fisher–John's melting point apparatus and are uncorrected. NMR spectra were obtained using a Varian Gemini 200 NMR spectrometer. Chemical shifts are in ppm with TMS as the internal standard. GC/MS and MS spectra were obtained either with a Hewlett–Packard (HP) 5997 mass spectrometer coupled to an HP5880A GC or a Shimadzu QP5050A mass spectrometer coupled to a Shimadzu GC-17A. Aldrich silica gel 60 Å (70 – 270 mesh) was used in chromatography. Elemental analysis was performed by Atlanta Microlab, Inc.

General procedure for synthesis of alkyl phenylglyoxylates:

Alkyl phenylglyoxylates were prepared by DCC esterification of the benzoylformic acid according to the literature procedure,[2] except for a modification in the separation step: after the precipitated urea was filtered off, the resulting solution was washed sequently with 10% acetic acid and 5% potassium carbonate and then dried over Na_2SO_4. After the solvent was removed under reduced pressure, the residue was passed through a small layer of silica gel using hexane as eluent.

2,2,2-Trichloroethyl Phenylglyoxylate. Yield – 45%. M.p. 32 – 33°C. ^{1}H NMR (200 MHz, CDCl$_3$) δ (ppm) 5.03 (s, 1H), 7.42 – 7.58 (m, 2H), 7.61 – 7.75 (m, 1H), 7.98 –

8.10 (m, 2H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 74.4, 93.9, 129.0, 130.0, 131.9, 135.3, 161.8, 184.5; CI–MS 281/283/285 (M+H$^+$), 245, 247, 165, 155, 145, 133, 106, 105, 91, 77, 51.

2,2,2-Trifluoroethyl Phenylglyoxylate. Yield – 78%. ^{1}H NMR (200 MHz, CDCl$_3$) δ (ppm) 4.77 (q, J_{H-F} = 8.2 Hz, 2H), 7.43 – 7.59 (m, 2H), 7.61 – 7.76 (m, 1H), 7.94 – 8.08 (m, 2H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 61.0 (q, J_{C-F} = 37.0 Hz), 122.5 (q, J_{C-F} = 275.7 Hz), 129.1, 130.0, 131.9, 135.5, 161.8, 184.3; CI–MS 233 (M+H$^+$), 219, 213, 181, 145, 133, 106, 105, 91, 77, 51. Anal. Calcd for C$_{10}$H$_7$F$_3$O$_3$: C, 51.74; H, 3.04. Found: C, 51.61; H, 3.10.

II. Data Processing

Time-resolved FTIR spectra contain the very large number of data points which effectively prevents the use of standard processing routines. The typical surface contains 125 000 to 2 500 000 points or 250 to 1500 individual spectra. In order to process them efficiently, a software utility *Tracer* was developed. This program imports and processes the raw data, and exports them in the format understood by the popular data processing packages. The following diagram demonstrates the *Tracer* organization:
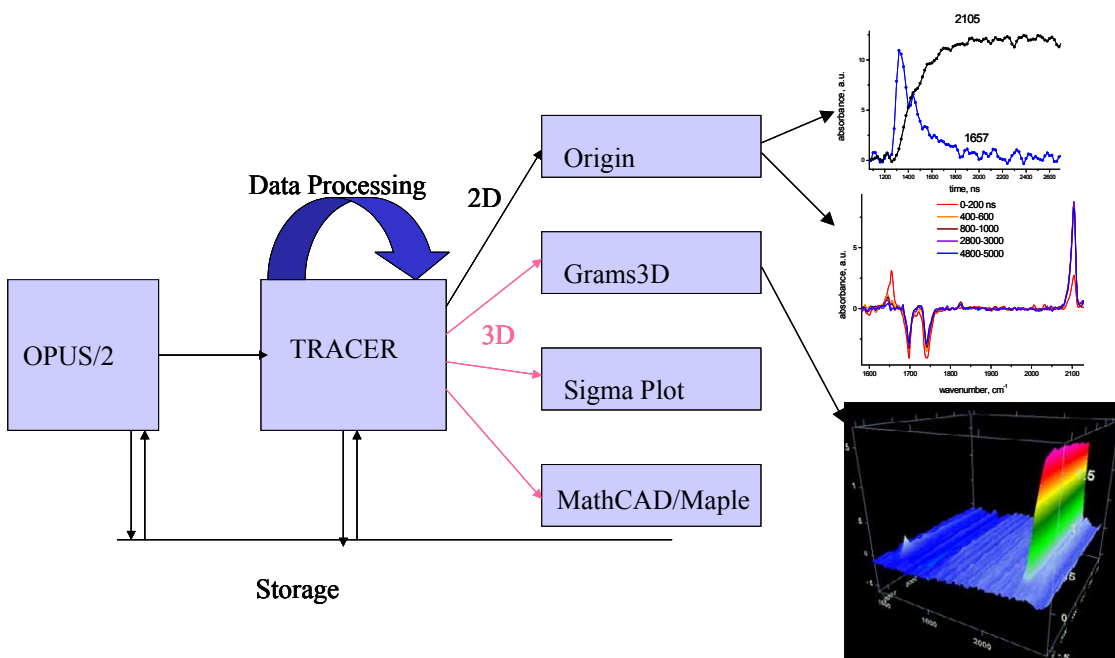
The data were presented as surfaces, colormaps and 2D spectra and kinetic profiles.

Low signal-to-noise ratio of the weak transient signals complicates their detection and characterization. Accordingly, in addition to conventional limiting of the spectral interval of interest and averaging, digital methods were used to reveal and analyze the weak transients. The baseline of 3D spectra was corrected using the procedure described previously [1(d)] and the resulting data were smoothed over 200 ns intervals. Then, the smoothed 3D surfaces were visualized as color maps. Normally, after this procedure the weak transients would clearly stand out against the background. Singular value decomposition (SVD) [5] was used to confirm the presence of the transient absorptions in the spectrum. The SVD was found to affect the lifetimes of the low-intensity transients though; therefore, it was not applied for kinetic analyses. [6]

After the approximate positions and amplitudes of the transients were obtained, a series of 2D spectra averaged over time intervals of 200 ns – 1μs were used to determine their exact positions. Finally, the kinetic traces were extracted from the original data and fit using non-linear least squares algorithm. The kinetic traces were fit using one exponential function each for rise and decay parts of the curve. This approach provides the information on the timescale on which the chemical events proceed and the rough estimation of the rate constants.
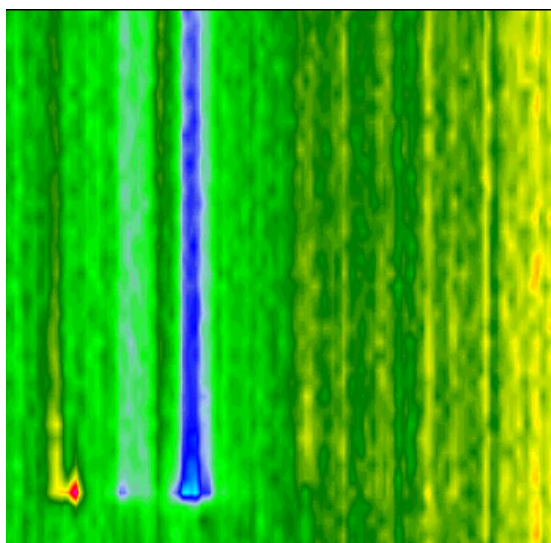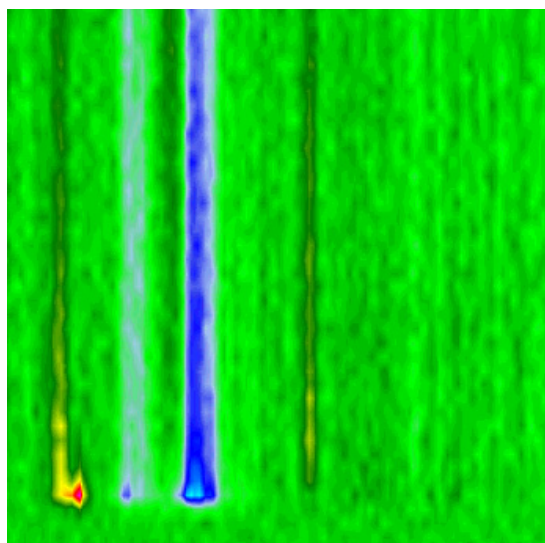
III. A representative colormap.
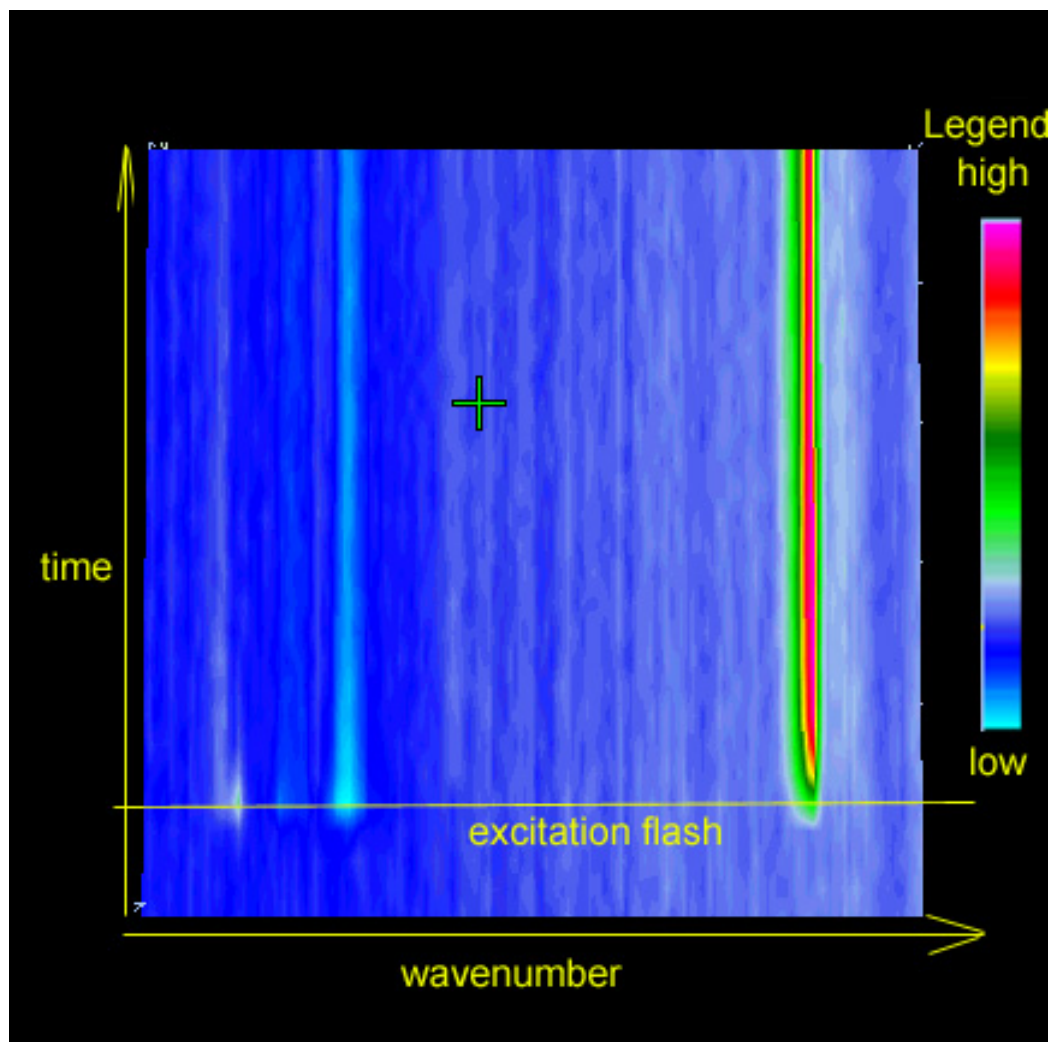
IV. The effect of data processing - smoothing (B) and baseline correction (C) – is revealed by the following three colormaps. The yellow arrow indicates the position of 1828 cm^{-1} transient.
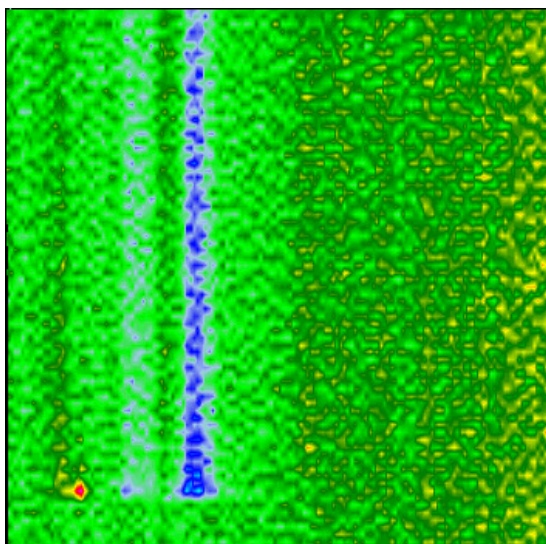
(A)

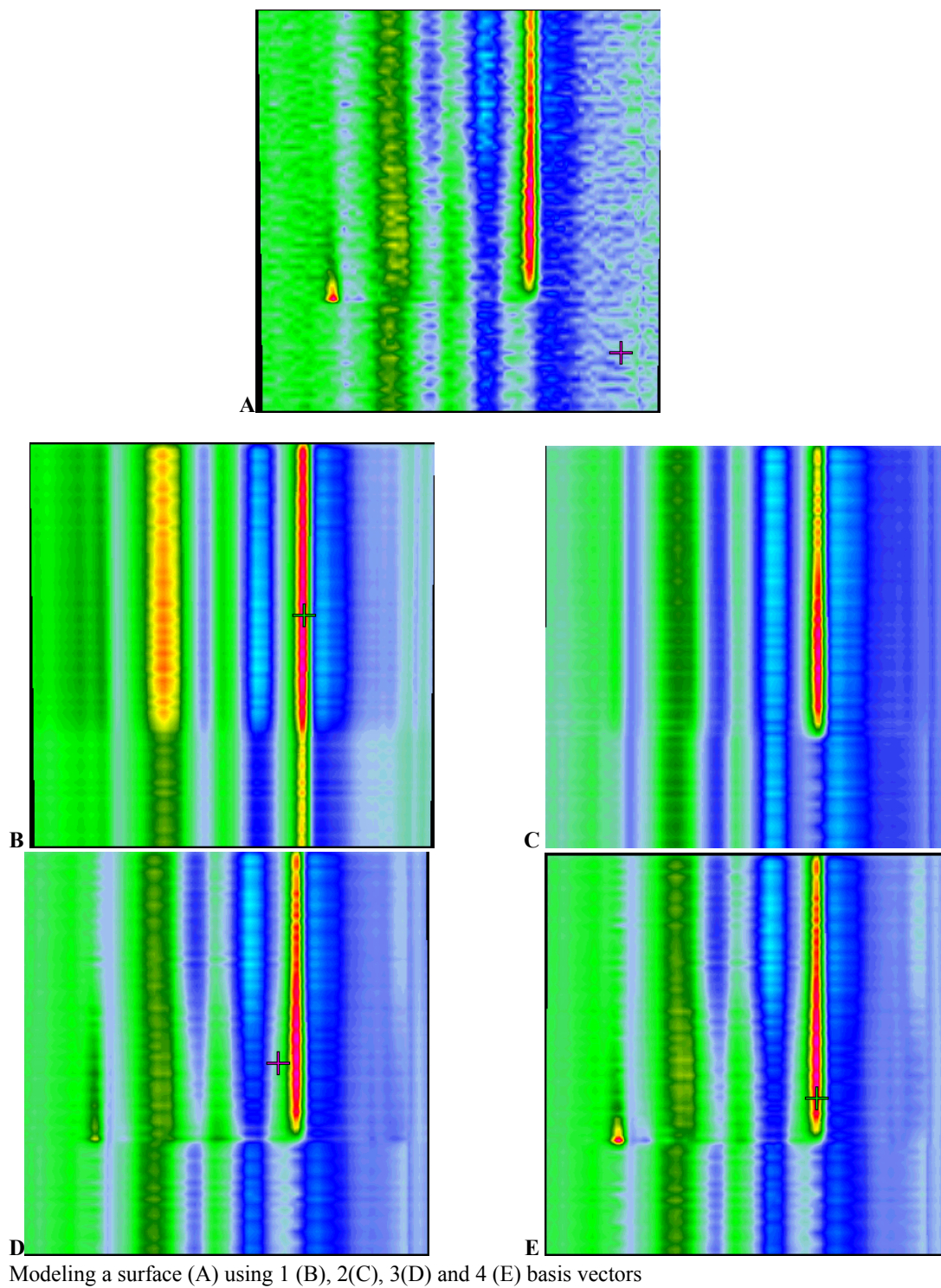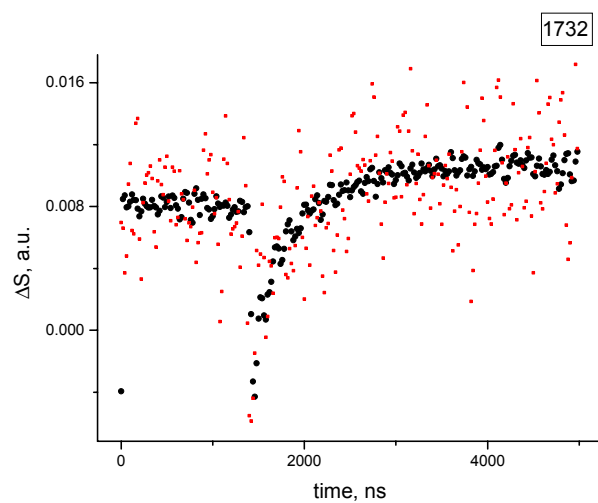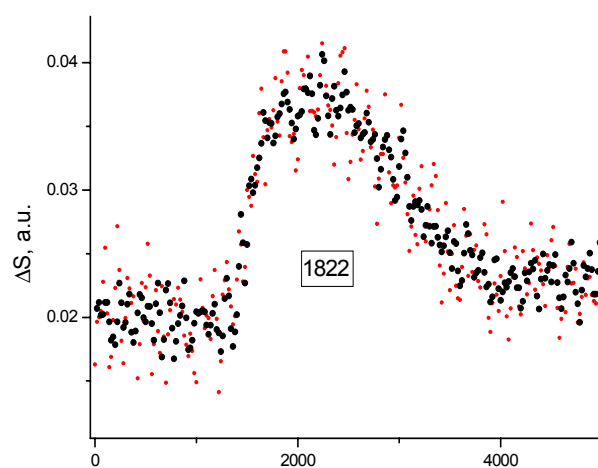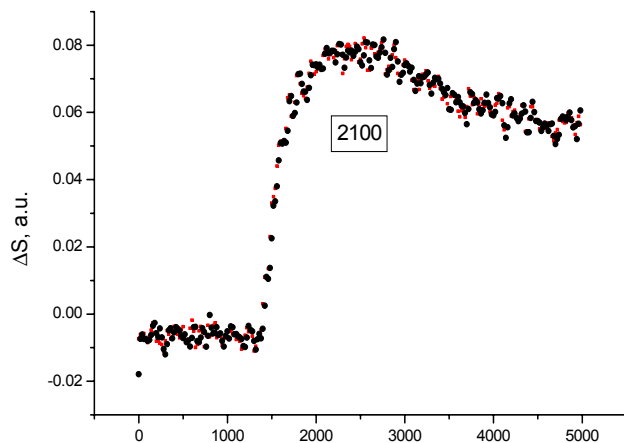(B)   (C)

(A) original data

(B) smoothed data

(C) smoothed and baselined data

V. Influence of Singular Value Decomposition on Noise Levels

Modeling a surface (A) using 1 (B), 2(C), 3(D) and 4 (E) basis vectors

VI. Influence of SVD processing on the weak and strong kinetics transients. The black dots represent the SVD-treated data and the red dots are the raw data.

VII. Influence of solvent on reaction pathway. FEPG in hexane (left) and dichloromethane (right) . Ketene (marked with arrow) is only observed in dichloromethane. The hexane product is a peak appearing around 1775 cm^{-1}.
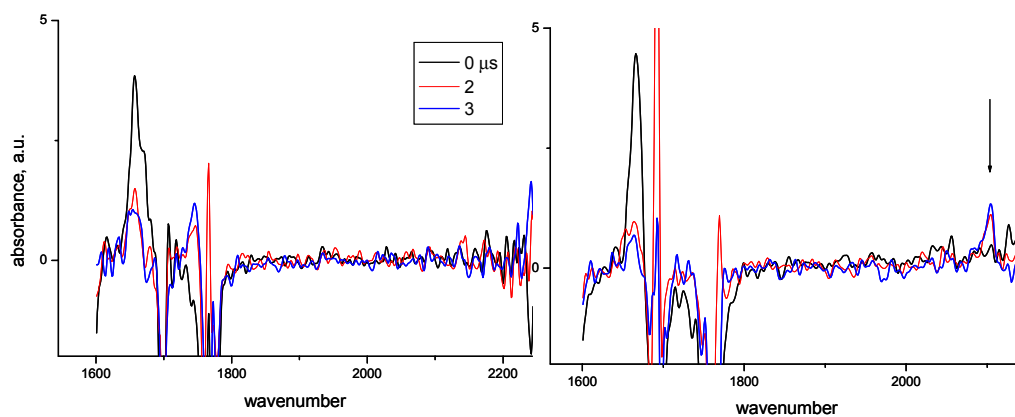
VIII. Bimolecular Ketene Formation. Quenching of the triplet state of EPG (left) and the corresponding decrease of the yield of ketene (right). Red: ethyl phenylglyoxylate in hexane; Blue: ethyl phenylglyoxylate in hexane with 1,4-cyclohexadiene.