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Photodegradation of Methyl Thioglycolate Particles as a Proxy for Organosulphur Containing Droplets

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Description of supplementary materiel

Fig S1 Optical images of a levitated droplet initially containing methyl thioglycolate before oxidation by air (a), after oxidation (b), and after 90-min of UV-Vis photolysis (c).

Fig.S2 First order kinetic of photodegradation of dimethyl dithiodiglycolate (DMTG) when irradiated with a broadband UV-Vis lamp (red) or with a 325-nm laser (blue). Data were corrected by the photon flux density.

Fig. S3 Raman spectra of pure methyl thioglycolate (MTG) in bulk in the region of 100-2700 cm^{-1} before and after 3.5, 7.5, 11.5 and 19.5 hours of irradiation with broadband UV-Vis light (300-800 nm)

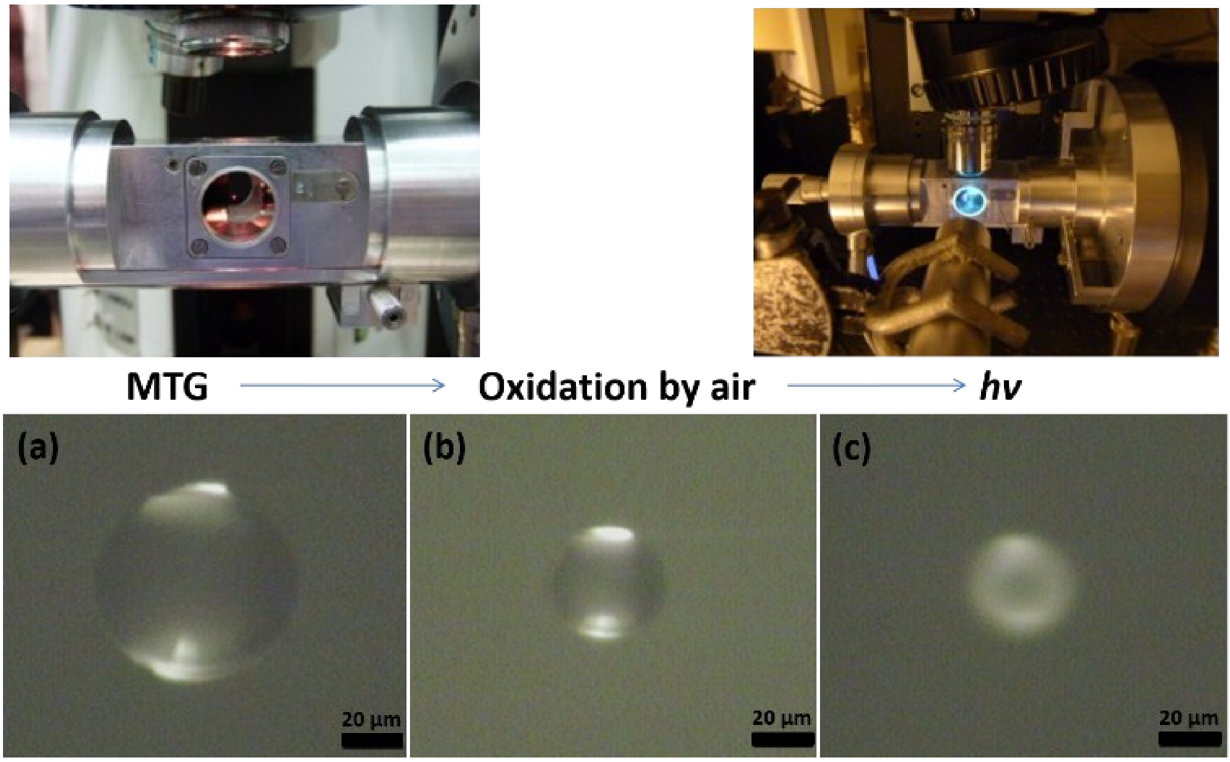
Fig. S4 Raman spectra of pure methyl thioglycolate (MTG) in bulk in the region of 100-2700 cm^{-1} before and after 3.5, 7.5, 11.5 and 19.5 hours of irradiation with broadband UV-Vis light (300-800 nm) in presence of O_2

Fig. S5 Raman spectra of an aqueous solution of methyl thioglycolate (MTG) in bulk in the region of 200-3000 cm^{-1} before and after 0, 16 and 32 hours of irradiation with broadband UV-Vis light (300-800 nm)

Table S1. Comparison of the slopes obtained by fitting of Raman intensities of DMTG and MA as a function of the irradiation time formed by photodegradation of MTG in bulk conditions

Table S2. Main species formed in the gas phase during irradiation with broadband UV-Vis light (300-800 nm) of the interface of an aqueous solution 0.3 M of MTG

Description and results of air-aqueous interface experiments



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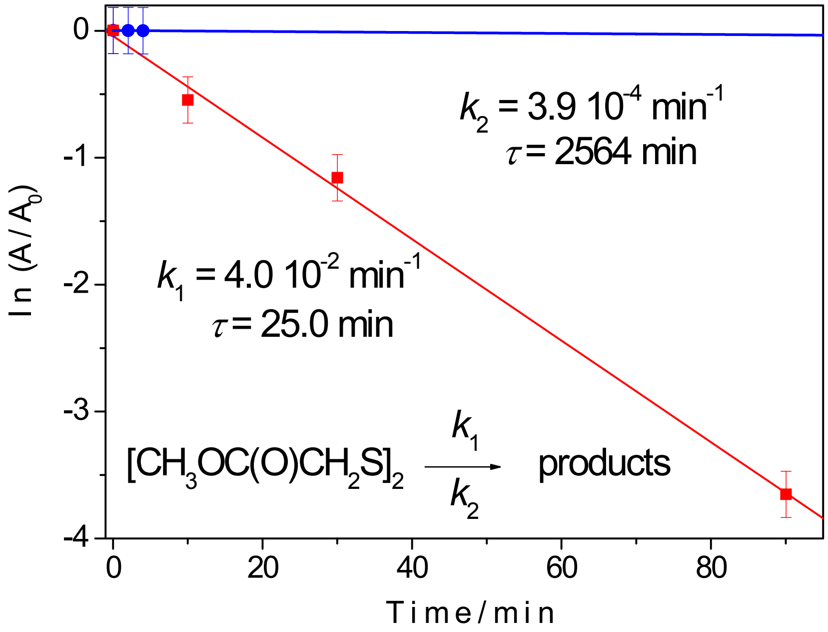

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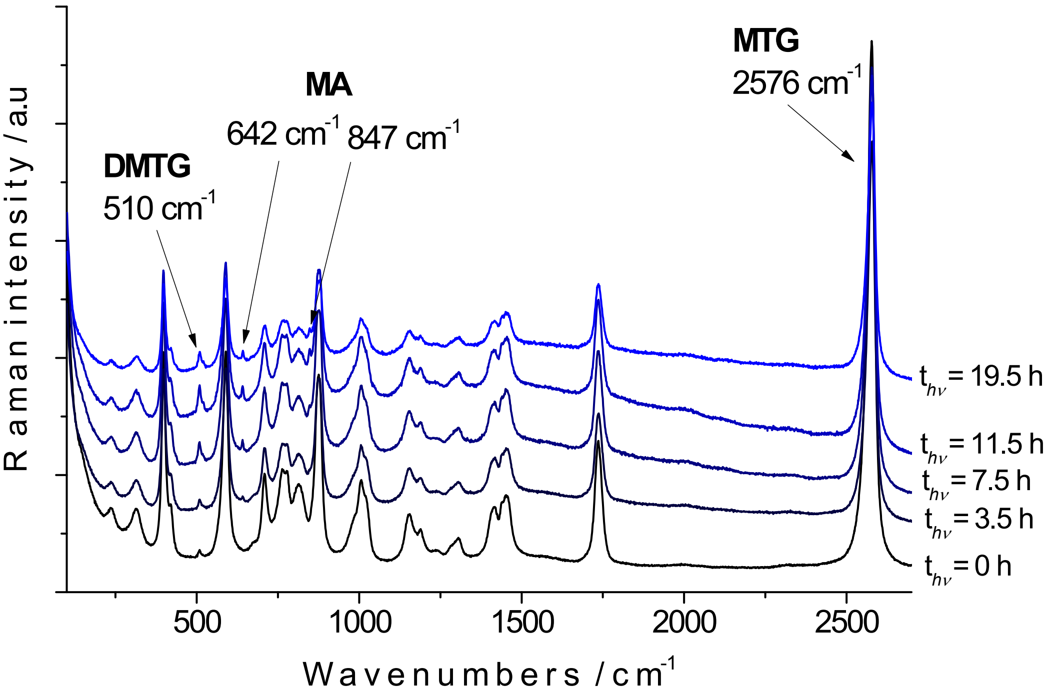

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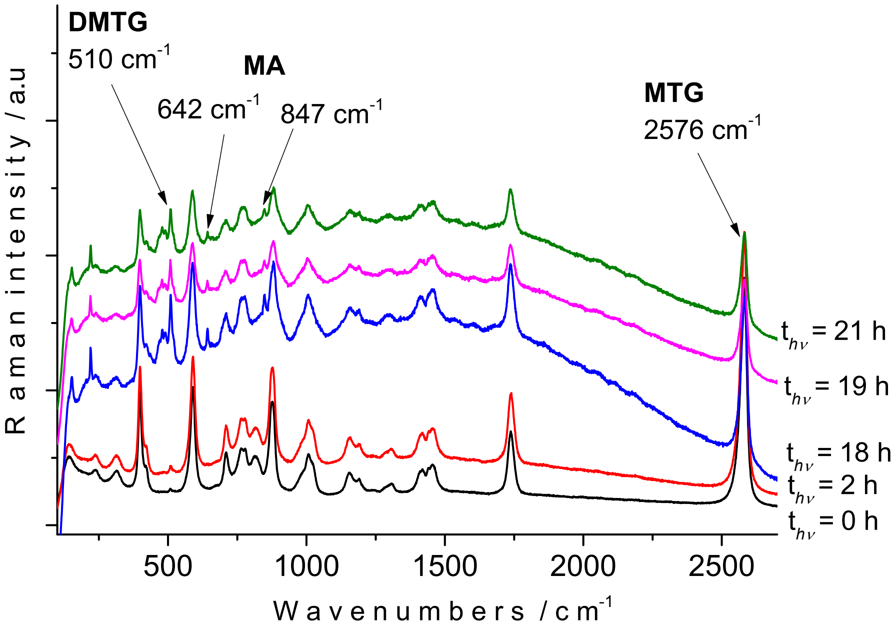

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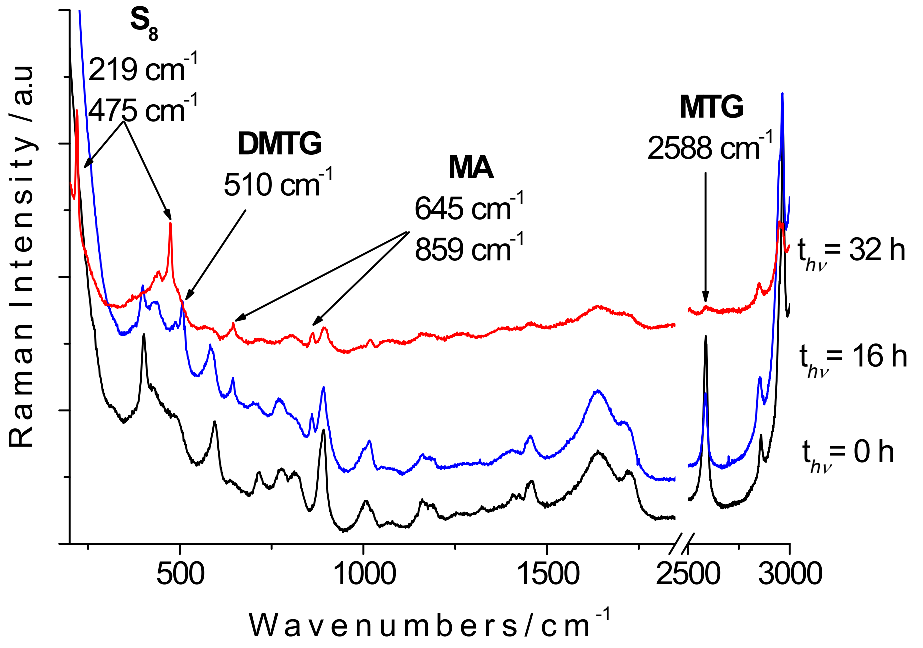

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Table S1. Comparison of the slopes obtained by fitting of Raman intensities of DMTG and MA as a function of the irradiation time formed by photodegradation of MTG in bulk conditions

	Slope*	
	DMTG	**MA**
MTG without O_2	1594.3	366.28
MTG with O_2	7739.9	1511.2
MTG aqueous solution	4284.6	3381.0

* The relative intensity of the products was calculated by normalisation of the spectra according the SH stretching mode of MTG.

Description and results of air/aqueous interface experiments

The gas-liquid interface of a 0.3 M aqueous solution of MTG was irradiated with a 150 W Xenon lamp (λ> 300 nm) in a quartz cell and the gas phase products were followed by PTR-ToF-MS.

Before irradiation, the PTR-MS spectra showed only the presence of gaseous MTG and dimeric form of methyl thioglycolate-$[MTG]_2$. The dimer was formed in the gas phase as recently described by our group.[1] In fact, due to its volatility, MTG (and also $[MTG]_2$) coexists in aqueous and gas phases and photoproducts could be formed from both gas phase photolysis and interface photolysis. Upon 30 minutes of irradiation, several products appeared, and were identified by their masses (m/z) and tentatively attributed as listed in Table S2. MTG and $[MTG]_2$ were detected after irradiation although the background content detected before irradiation was subtracted. This was mainly explained by slight heating of the surface during irradiation process. The main secondary product identified was thioformaldehyde (CH_2S). The formation of thioformaldehyde may likely have proceeded through fragmentation of MTG and -$[MTG]_2$ molecules using PTR-MS. However, regarding the total amount detected after irradiation, the formation of CH_2S trough irradiation of the surface cannot be totally excluded. Both condensed and gas phase MTG photochemistry have contributed to the formation of methyl acetate as demonstrated in this work and in previous reported work.[30] Thus, we have ascertained the formation of MA also from the interface. The formation of S-rich molecules i.e., $C_4H_{10}S$, C_3H_8S, CH_4S, C_2H_6S, C_4H_8S, and C_2H_2S were likely due to the fragmentation of MTG and $[MTG]_2$ molecules within PTR-MS. $C_2H_4O_2$ that can be attributed to acetic acid probably resulted from fragmentation of methyl acetate. Finally, Methanethioic acid (CH_2OS) would be the only secondary product originated from the interface irradiation since it was not detected neither in gas phase nor in condensed phase.

Table S2. Main species formed in the gas phase during irradiation with broadband UV-Vis light (300-800 nm) of the interface of an aqueous solution 0.3 M of MTG

Molecular weight / uma	molecular formula (Tentative species)	Concentration / ppb
46.995	CH_2S (Thioformaldehyde)	88.0
74.080	$C_3H_6O_2$ (Methyl acetate)	8.0
211.027	$C_6H_{12}O_4S_2$ (MTG dimer)	8.0
91.057	$C_4H_{10}S$	6.0
61.011	$C_2H_4O_2$	4.5
62.989	CH_2OS (Methanethioic acid)	2.2
77.042	C_3H_8	1.0
49.011	CH_4S (Methanethiol)	0.7
63.026	C_2H_6S (DMS)	0.7
89.042	C_4H_8S	0.6
58.995	C_2H_2S (Thioketene)	0.5

References

1. Y. B. Bava, L. M. Tamone, L. C. Juncal, S. Seng, Y. A. Tobón, S. Sobanska, A. L. Picone, and R. M. Romano. *J. Photochem. Photobiol. A,* 2017, **344**, 101–107