Gas-Phase Photochemical Overall H₂S Splitting by UV Light Irradiation

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Abstract: Upon irradiation at 254 nm in the gas phase H₂S splits into stoichiometric amounts of H₂ and S with quantum efficiency close to 50 %. No influence of the presence of CH₄ and CO₂ (typical components in natural gas and bio-gas in where H₂S is an unwanted component) on the efficiency of overall H₂S splitting was observed. A mechanism for the H₂ and S formation is proposed.
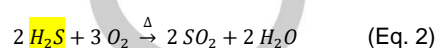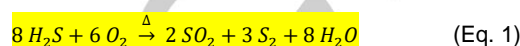
Introduction

The Hydrogen sulfide is a toxic and malodorous gas formed in the anaerobic fermentation and *decomposition* of organic matter that is present in bio-gas, most natural gas wells and in volcanic eruptions. Besides natural origin, the presence of S compounds in fossil oils and the environmental problems associated to their combustion makes necessary harsh hydrodesulfuration treatments of fuels that is also a massive source of H₂S at the refineries.[1]

Different methods are employed for H₂S trapping and removal from natural and bio gas, however, those based on its solubilization in aqueous basic media are the most widely used.[2] This creates the problem of treating large volumes of waste waters, being desirable methodologies to transform H₂S directly in the gas phase without interference of the presence of a large excess of CH₄, CO₂, moisture or other gases. In this way, it should be possible the selective H₂S decomposition in those streams in which this gas is usually present without the need of isolation. The most widely industrial application of H₂S is as a source of elemental sulphur that is used in a large percentage for the synthesis of sulfuric acid.

The classical industrial process for large scale conversion of H₂S in the over hundred-years old Claus process (Eq. 1). In this process, H₂S is converted in two steps into elemental S and H₂O. The first step of the Claus process consists in the controlled thermal oxidation of H₂S to SO₂ and H₂O at temperatures above 850 °C (Eq. 2). A subsequent catalytic step with activated aluminum (III) or titanium (IV) oxides yields elemental S and H₂O (Eq. 3).

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$$8\ H_2S + 6\ O_2 \xrightarrow{\Delta} 2\ SO_2 + 3\ S_2 + 8\ H_2O \qquad \text{(Eq. 1)}$$

$$2\ H_2S + 3\ O_2 \xrightarrow{\Delta} 2\ SO_2 + 2\ H_2O \qquad \text{(Eq. 2)}$$

$$2\ H_2S + SO_2 \xrightarrow{Cat.} 3\ S + 2\ H_2O \qquad \text{Cat: } Al_2O_3 \text{ or } TiO_2 \qquad \text{(Eq. 3)}$$

Although the Claus process is a well proven technology, it has several drawbacks including the need to purify and capture H₂S from the effluents, the capital investment required for the two-step processes, the high temperatures required in the thermal step (Eq. 2) and the severe catalyst deactivation of the second step (Eq. 3) among others.

A conceptual limitation of the Claus reaction is the waste of part of the chemical energy stored in the H₂S bonds that is used to provide the heat needed in the process, leading to the formation of H₂O.[3] An alternative to the Claus process should consider the possibility to convert H₂S directly in the gas phase without interference of other gases such as CO₂, CH₄, N₂ and to split the molecule into S and high-added value H₂. Considering the massive quantities of H₂S available and that this gas can be considered as a renewable raw material when derived from anaerobic biomass fermentation, it would be highly desirable if this chemical can serve as a source of H₂ in addition than as a source of elemental S₈. Several methods have been already described in the literature for the production of H₂ from H₂S, such as thermal decomposition, electrochemical, plasmachemical and photocatalytic,[4] but most of them result in the sacrificial overoxidation of elemental S to sulfite and sulfate.

The photocatalytic decomposition of H₂S into H₂ in gas or liquid phases has been widely studied using semiconductors (TiO₂, ZnO, CdS, etc) as photocatalysts and precious noble metals (Pt, Ru, etc) as co-catalyst upon UV-Vis light irradiation.[5] However, low concentration of H₂S have been frequently used (normally tens of ppm) resulting in the formation of sulphur containing acids that may cause severe photocatalyst deactivation as consequence of their deposition on the photocatalyst surface. The yields of elemental sulphur is frequently ignored and not considered.

Most of the photochemical studies have only been performed in aqueous phase, but not in the gas phase.[6] Precedents in the gas-phase splitting of H₂S reported in the 80s have dealt with the photophysics of H-S bond and the form how the excess of energy of the excited state is dissipated in the process.[7] However, at that moment no attention was paid to the direct gas-phase H₂S splitting as simultaneous source of renewable H₂ and elemental S and the nature and yields of these reaction products. Considering the current interest in photochemical H₂ generation from overall H₂O splitting and the large availability of H₂S, the

focus of the present manuscript is to determine the efficiency and product distribution of the direct, overall H_2S splitting in gaseous mixtures, in the absence of any sacrificial agent upon direct UV (254 nm) irradiation without the presence of any catalyst or photocatalyst. The advantages of this photochemical H_2S splitting are the simultaneous production of H_2 and S without additional heating (temperature below 80 ºC), in the absence of catalysts and being compatible with a wide range of H_2S concentrations diluted in other gases (i.e. CH_4, CO_2 or N_2, etc) that simulate mixtures that can be present in real natural gas streams and biogas. Thus, no separation or purification step is necessary, eliminating the environmental concerns raised by sulfur-containing waste waters.

Results and Discussion

Initially, the overall photochemical H_2S was carried out in the total absence of O_2 by irradiating H_2S in N_2 mixtures at different concentrations and 1 bar total pressure in a close reactor of 50 ml total volume upon *quasi* monochromatic 254 nm light irradiation from a low-pressure Hg lamp. The temporal profiles of H_2 production and H_2S disappearance under these conditions are presented in Fig. 1.

As can be observed in Fig. 1 (top), irradiation of a gas mixture containing H_2S in 9.5 vol% in N_2 leads to complete H_2S conversion, obtaining H_2 in the expected stoichiometric amounts. In a similar way, complete H_2S conversion was achieved for 1.5 vol% and 3.6 vol.% concentrations diluted in N_2 gas in approximately 8 h, as can be seen in Fig. 1 (bottom) and Table 1. In all cases, deposition on the cold walls of the photoreactor of a white-yellow solid material identified as elemental sulphur was also observed (the cold parts of the reactor have been indicated in the Scheme presented in Figure SI1 in supplementary information). Note that although the reaction was not heated, the temperature inside the photoreactor reached gradually a maximum value about 80 ºC, due to heat dissipation of the Hg lamp and the coldest parts of the system were those not exposed to the lamps that were where S deposited. Quantification of the solid was also in agreement with the complete conversion of H_2S into S. Experiments of the overall H_2S splitting were performed several times, measuring essentially identical temporal profiles for H_2 formation and H_2S disappearance (see error bars in Fig. 1 data points), showing that the process is reliable and results in the complete overall splitting of H_2S into H_2 and elemental S.

Control experiments in dark submitting the reactor at 80 ºC were carried out, but no decomposition of H_2S, generation of H_2 or deposition of S was detected under these conditions.

Similarly to the previously commented experiments of overall H_2S splitting in N_2, the UV photochemical H_2S splitting was also carried out in other mixtures simulating compositions of effluents in where H_2S can be present, such as natural gases containing CH_4, as predominant component, and biogas containing CO_2 and N_2, at two different proportions of H_2S. The purpose is to show that the overall H_2S splitting can take place without

interference of these gases, which have been found to do not exhibit absorption in this spectral region (254 nm) and, therefore,
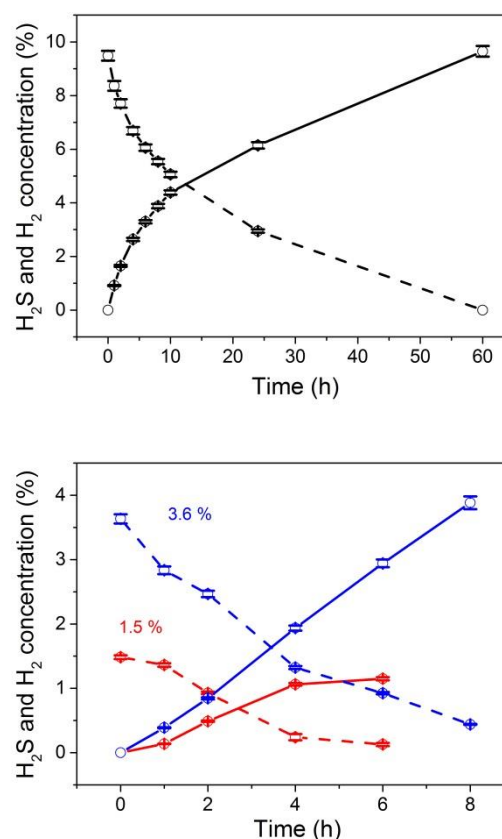

Figure 1. H_2 (solid lines) and H_2S (dashed lines) evolution at (top) 9.5 vol.% (black) and (bottom) 3.6 vol.% (red) and 1.5 vol.% (blue) initial H_2S concentration in N_2 upon Hg lamp illumination at 254 nm. The plot is the average of three independent measurements with variation of the experimental data lower than 5%.

Table 1. Results of the irradiation at 254 nm of gas mixtures containing H_2S and the final content of H_2 and H_2S. Note that in all cases S was deposited on the cold part of the photoreactor in the expected stoichiometric amount.

Nº	Gas composition before reaction (Vol.%)				Time (h)	Gas composition after reaction (Vol.%)	
	H_2S	CH_4	CO_2	N_2		H_2	H_2S
1	6	0	50	44	24	5.74±0.4	0.23
2	6	50	0	44	24	5.64±0.7	0.19
3	2	0	66	32	6	2.15±0.2	0.08
4	2	66	0	32	6	2.44±0.5	0.21
5	9.5	0	0	90.5	60	9.55±0.5	0
6	3.6	0	0	96.4	8	3.68±0.5	0.44
7	1.5	0	0	98.5	6	1.15±0.3	0.13

the H_2S decomposition process could be applicable in most of the real gases without the need of H_2S purification. The results are summarized in Table 1. As can be seen in Table 1, the presence of CH_4 and CO_2 in large concentrations respect to H_2S, corresponding to compositions of real mixtures, does not interfere in the overall H_2S splitting, regardless H_2S concentrations (from 2 to 6 %), achieving complete removal of H_2S in few hours under our irradiation conditions, H_2S exhibiting the same photochemical behavior as in the absence of these gases. The time required for complete H_2S removal increases along its initial concentration. This is understandable considering that neither CH_4 nor CO_2 has absorption bands in the UV above 200 nm. Note that the reaction proceeds to completion because elemental sulphur is deposited in the cold parts of the photoreactor and not in the illuminated (hot) parts that are transparent during the whole process.

This selectivity for overall H_2S splitting in the photochemical reaction in the presence of other gases can be easily explained considering the absorption spectra of CH_4 and CO_2. It has been widely reported that CO_2 do not absorb light at wavelengths larger than 200 nm[8], while CH_4 and N_2 are transparent and do not absorb UV light at all. In contrast, H_2S has an absorption from 270 nm into the deep UV. Fig. 2 presents the UV absorption spectrum of H_2S gas. The sharp absorption lines with fine structure observed are characteristic of gas-phase molecules, while the broad absorption band underneath indicates the occurrence of some H_2S aggregation at this concentration even in the gas phase.

Considering the UV absorption spectrum of H_2S shown in Fig. 2, the overall H_2S splitting was also tested at longer wavelengths. Specifically, the photochemical H_2S splitting was carried out at 300 nm and 354 nm. A mixture of 10.8 vol.% of H_2S in N_2 was used in this study, monitoring the H_2 evolution and H_2S disappearance as depicted in Fig. 3.

As can be observed in Fig. 3, H_2S irradiation at 300 or 354 nm did not allow the detection of measurable H_2 amounts. These negative results contrast with those observed upon 254 nm irradiation, where H_2 evolution occurs. This dependence of the irradiation wavelength on the photochemical overall H_2S splitting can be easily rationalized based on the UV absorption spectrum of H_2S shown in Fig. 2 that does not present significant photon absorption beyond 270 nm.

The quantum yield for light-induced H_2 generation was calculated by dividing the moles of H_2 formed per photons absorbed by H_2S for mixtures of 9.5 vol.% H_2S in N_2 upon 254 nm irradiation. By determining the lamp flux using a calibrated photodiode, it was found that 0.53 H_2 molecules were produced per photon absorbed when UV irradiation at 254 nm was used, and only 0.016 and $2.6\cdot10^{-5}$ for 300 and 354 nm, respectively. The absolute quantum yield at 254 nm is around the theoretical limit of 0.5. This quantum yield value means that formation of a H_2 molecule is a process requiring two photons. A simple rationalization of this quantum yield is that each photon would break a H-S bond with 100% efficiency. This hypothesis would be compatible with the prior observation of HS· radical in the photolysis of H_2S.[6, 7] This implies that when using 254 nm,

absorption of a single photon of such energy must lead to the cleavage of one S-H bond, resulting in the generation of one H atom and HS·. Formation of H_2 from H· would require, then, another photon, either by splitting H-S· or by reaction of H· with photoexcited H_2S, among other possibilities. Scheme 1 summarizes the proposal. In any case, a quantum yield of 0.53±0.01 indicates a very high efficiency of photochemical H-S bond cleavage. In spite of this high quantum yield, an estimation of electricity costs based on the quantum yield value at 254 nm (around 0.5), the photon flux of the 45 W Hg lamp (6.09×10^{15} photons×s^{-1}), assuming a cost of 0.1 €×kwh^{-1} gives a value of 0.01 g×€$^{-1}$ for H_2 and 0.18 g×€$^{-1}$ for S. This cost is mainly limited by the efficiency of the electricity to light conversion. Lamps higher yield of emitted photons per consumed W would be highly desirable.
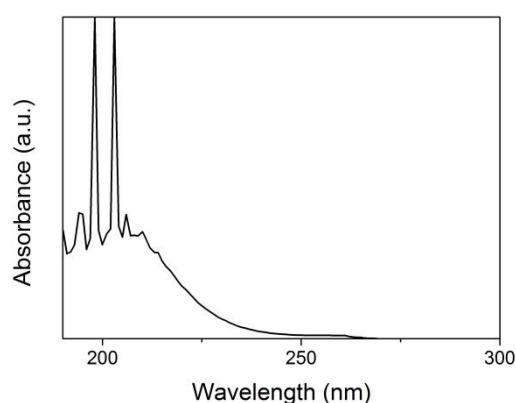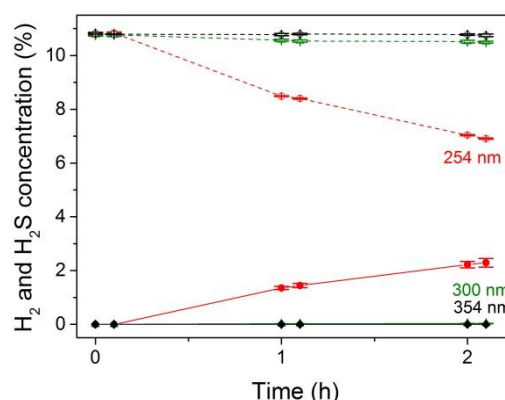

Figure 2. Gas-phase UV spectrum of 9.5 vol.% of H_2S in N_2.

Figure 3. Temporal profiles of H_2 generation (solid lines) and H_2S disappearance (dashed lines) in mixtures containing an initial 10.8 vol.% H_2S concentration upon irradiation with quasi monochromatic light of different wavelengths: 254 nm (red), 300 nm (green) and 354 nm (black). Note that the green and black lines essentially overlap giving zero H_2 production.

In order to further investigate the reaction mechanism looking for the detection of possible excited states or intermediates, gas-phase transient absorption spectroscopy experiments in the microsecond time scale were carried out using a Nd:YAG laser at 266 nm excitation wavelength. Unfortunately, no transients could be detected, including the attempts to trap ·SH radicals or S atoms by conjugated dienes that could lead to detectable

transients.[9] Considering the instrument response of our instrument (about 20 ns), the failure to detect any intermediate, even at short delay times, probably indicates that transient species in gas phase do not absorb in the wavelength range available to our laser system. Alternatively, quenching of ·SH was attempted by performing 254 nm irradiation of H_2S in the presence of cyclohexene. The ability of alkenes to undergo electrophilic radical additions by thiols in high yields at low temperature is well documented in the literature.[10] Analysis of the reaction products by mass spectroscopy revealed the presence of dicyclohexyl sulfide and 1,2-dicyclohexyldisulfane (see structures in Scheme 1). Specifically, no evidence of the presence of cyclohexene thiirane or cyclohexanethiol was observed.

Although less informative, the transient absorption spectrum study was also carried out in aqueous solution by irradiating
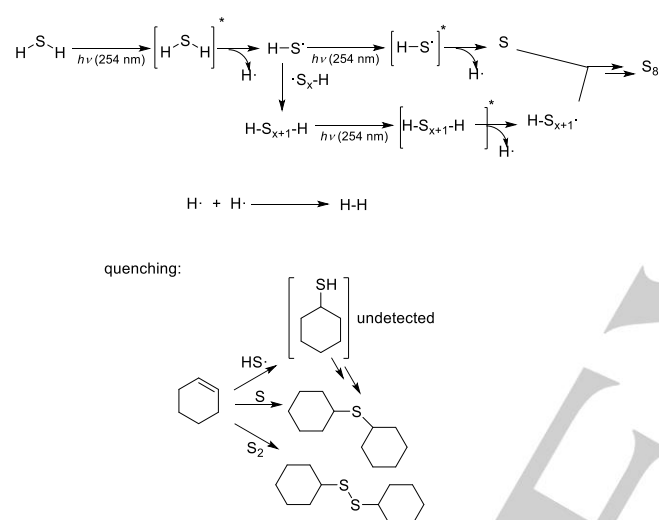
Scheme 1. Proposed mechanism for the overall H_2S splitting upon 254 nm light irradiation showing the need of two photons for the generation of each H_2 molecule and structures of the S-cyclohexene adducts observed in the quenching study.

diluted solutions of NaHS (pH 7 – 8) at 266 nm under inert atmosphere. Under these conditions the transient absorption spectrum (Fig. 4) shows two main bands centered at 280 and 380 nm, with lifetimes in the range from 1 to 100 µs. This transient spectrum agrees with a previous report on the photolysis of H_2S in aqueous solution and assigned to HS_2^- species.[11] Further evidence for this assignment was obtained here by measuring the steady-state absorption spectrum of Na_2S_2 in aqueous solution that is a stable disulfide commercially available. A band at 380 nm was recorded for Na_2S_2. Therefore, we can assume that the transient absorption signal found in the present case correspond to S_2^{2-} ions. Thus, even in water, generation of S radical species resulting in S-S coupling is likely the occurring process. Radicals should be even more favored in gas phase. That means that in the gas phase, in absence of solvent and other ions the formation of S radicals should be favored.

Although the conditions in the gas phase are different, the transient absorption spectrum in aqueous solution shows the tendency of sulphides to form promptly S-S bonds, a fact that is well known in sulphur chemistry and would occur even faster in the gas phase, where sulphide ions cannot be involved.
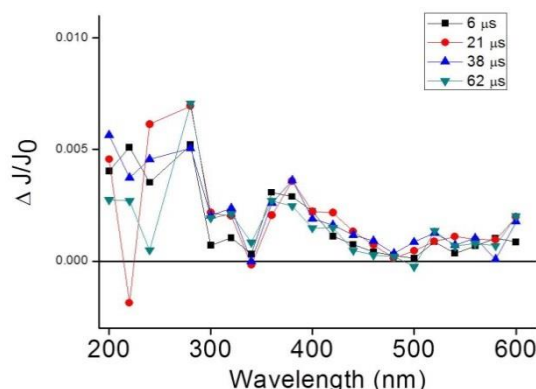
Figure 4. Transient absorption spectra of Na_2S in aqueous solution (pH 7 – 8) upon 266 nm laser excitation at different times.

Conclusions

The photochemical H_2S splitting with UV light has been demonstrated to occur high efficiently in the gas phase in the absence of catalysts or photocatalysts at near room temperature, rendering H_2 and S in quantitative yields. This process exhibits high quantum yield for H_2 generation of 0.53±0.1 upon irradiation at 254 nm. Moreover, the presence of different gases even at high concentrations, typically found in natural gas or gas from biodigestors, does not affect the efficiency of the photochemical reaction. Trapping experiments are compatible with the generation of reactive mono and disulphur species in the gas phase in detectable amounts.

Experimental Section

The reactions were carried out in a close cylindrical reactor made of Suprasil® quartz with total volume of 51 ml. The temperature and pressure inside the reactor were controlled through a thermocouple and manometer, respectively. The reactor was filled with N_2 and H_2S at different concentrations at a final pressure of 1 bar. Other gases can also be introduced into the system. Three Hg lamps (Ushio G8TS) with a nominal power of 45 W each were used as a source of UV radiation. These lamps emit quasi monochromatic radiation at a wavelength of 254.5 nm with a power of 4 W. In addition, a small power percentage is emitted in the visible region and the rest is lost as heat. The reaction temperature increase over time up to a maximum value of 80 ºC reached in about 15 min. and is solely due to the heat emitted by the lamps with no additional heating. Both the substrates and gaseous reaction products were analysed by a micro-GC equipped with two Agilent columns (PPQ and MS5A) and two TCD. Sulphur analysis was performed by exhaustive washings of the reactor with CS_2 and the solution was analyzed by gas chromatography in a Varian 3900 apparatus equipped with a TRB-5MS column (5% phenyl, 95% polymethylsiloxane, 30 m x 0.25 mm x 0.25 µm, Teknokroma), whereby sulphur was quantified to be formed in stoichiometric amounts respect the initial H_2S employed using dodecane as standard and the corresponding calibration plot. Quantum yields were determined by measuring the photon flux of each excitation lamp with a calibrated Si photodiode (Edmund Optics Si detector #53-375) and

dividing the number of H₂ molecules formed by the corresponding number of emitted photons. Trapping of sulphur species was performed by irradiating under the same conditions a mixture of 10 wt% of H₂S diluted into N₂ after having added into the reactor 100 ml of cyclohexene (b.p. 60 °C). At the end of the reaction, the reactor walls were extracted with diethyl ether and the extract injected into a GC apparatus having a 30 m column of 5% crosslinked phenyl methyl silicone using He as carrier gas and a FI detector or quadrupole mass detector. Dicyclohexyl sulphide and 1,2-dicyclohexyldisulfane were identified based on their mass spectra.

Transient absorption spectra were recorded using the forth harmonic of a Q switched Nd:YAG laser (Quantel Brilliant, 266 nm, 15 mJ/pulse, 7 ns fwhm) coupled to a mLFP-122 Luzchem miniaturized detection equipment. This transient absorption spectrometer includes a 300 W ceramic xenon lamp, 125 mm monochromator, Tektronix TDS-2001C digitizer, compact photomultiplier and power supply, cell holder and fiber-optic connectors, computer interfaces, and a software package developed in the LabVIEW environment from National Instruments. The laser flash generates a 5 V trigger pulses with programmable frequency and delay. The rise time of the detector/digitizer is ∼3 ns up to 300 MHz (2.5 GHz sampling). The monitoring beam is provided by a ceramic xenon lamp and delivered through fiber-optic cables. The laser pulse is probed by a fiber that synchronizes the LFP detection system with the digitizer operating in the pretrigger mode. Transient spectra in the gas phase were recorded using 10 mm × 10 mm quartz cells of 4 mL capacity that were capped with a rubber septum and flushed for at least 15 min with a flow of H₂S diluted in N₂ at atmospheric pressure. For solution experiments the same cell containing an aqueous solution of Na₂S (pH 7.8, optical density of 0.2 at 266 nm) that were bubbled for 15 min with argon.

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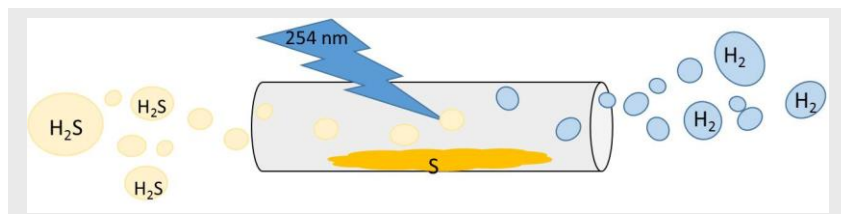
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