
The final publication is available at
https://doi.org/10.1002/cssc.201700294

Copyright John Wiley & Sons

Additional Information
Gas-Phase Photochemical Overall H$_2$S Splitting by UV Light Irradiation


Abstract: Upon irradiation at 254 nm in the gas phase H$_2$S splits into stoichiometric amounts of H$_2$ and S with quantum efficiency close to 50%. No influence of the presence of CH$_4$ and CO$_2$ (typical components in natural gas and bio-gas in where H$_2$S is an unwanted component) on the efficiency of overall H$_2$S splitting was observed. A mechanism for the H$_2$ 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 desulfuration treatments of fuels that is also a massive source of H$_2$S at the refineries.[1]

Different methods are employed for H$_2$S 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 H$_2$S directly in the gas phase without interference of the presence of a large excess of CH$_4$, CO$_2$, moisture or other gases. In this way, it should be possible the selective H$_2$S decomposition in those streams in which this gas is usually present without the need of isolation. The most widely industrial application of H$_2$S 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 H$_2$S in the over hundred-years old Claus process, (Eq. 1). In this process, H$_2$S is converted in two steps into elemental S and H$_2$O. The first step of the Claus process consists in the controlled thermal oxidation of H$_2$S to SO$_2$ and H$_2$O at temperatures above 850 °C (Eq. 2). A subsequent catalytic step with activated aluminum (III) or titanium (IV) oxides yields elemental S and H$_2$O (Eq. 3).

$$8 \text{H}_2\text{S} + 6 \text{O}_2 \xrightarrow{\Delta} 2 \text{SO}_2 + 3 \text{S}_2 + 8 \text{H}_2\text{O} \quad \text{(Eq. 1)}$$

$$2 \text{H}_2\text{S} + 3 \text{O}_2 \xrightarrow{\Delta} 2 \text{SO}_2 + 2 \text{H}_2\text{O} \quad \text{(Eq. 2)}$$

$$2 \text{H}_2\text{S} + \text{SO}_2 \xrightarrow{\text{cat.}} 3 \text{S} + 2 \text{H}_2\text{O} \quad \text{Cat: Al}_2\text{O}_3 \text{ or TiO}_2 \quad \text{(Eq. 3)}$$

Although the Claus process is a well proven technology, it has several drawbacks including the need to purify and capture H$_2$S 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 H$_2$S bonds that is used to provide the heat needed in the process, leading to the formation of H$_2$O.[1] An alternative to the Claus process should consider the possibility to convert H$_2$S directly in the gas phase without interference of other gases such as CO$_2$, CH$_4$, N$_2$ and to split the molecule into S and high-added value H$_2$. Considering the massive quantities of H$_2$S 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 H$_2$ in addition than as a source of elemental S. Several methods have been already described in the literature for the production of H$_2$ from H$_2$S, such as thermal decomposition, electrochemical, plasmachemical and photocatalytic,[4,5] but most of them result in the sacrificial overoxidation of elemental S to sulfate and sulfite.

The photocatalytic decomposition of H$_2$S into H$_2$ in gas or liquid phases has been widely studied using semiconductors (TiO$_2$, 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 H$_2$S 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 H$_2$S 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 H$_2$S splitting as simultaneous source of renewable H$_2$ and elemental S and the nature and yields of these reaction products. Considering the current interest in photochemical H$_2$ generation from overall H$_2$O splitting and the large availability of H$_2$S, the
focus of the present manuscript is to determine the efficiency and product distribution of the direct, overall H$_2$S 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$_2$S splitting are the simultaneous production of H$_2$ and S without additional heating (temperature below 80 °C), in the absence of catalysts and being compatible with a wide range of H$_2$S 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$_2$S was carried out in the total absence of O$_2$ by irradiating H$_2$S 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$_2$S disappearance under these conditions are presented in Fig. 1.

As can be observed in Fig. 1 (top), irradiation of a gas mixture containing H$_2$S in 9.5 vol% in N$_2$ leads to complete H$_2$S conversion, obtaining H$_2$ in the expected stoichiometric amounts. In a similar way, complete H$_2$S 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 S11 in supplementary information). Note that although the reaction was not heated, the temperature inside the photoreactor reached gradually a maximum value about 80 °C, 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$_2$S into S. Experiments of the overall H$_2$S splitting were performed several times, measuring essentially identical temporal profiles for H$_2$ formation and H$_2$S disappearance (see error bars in Fig. 1 data points), showing that the process is reliable and results in the complete overall splitting of H$_2$S into H$_2$ and elemental S.

Control experiments in dark submitting the reactor at 80 °C were carried out, but no decomposition of H$_2$S, generation of H$_2$ or deposition of S was detected under these conditions.

Similarly to the previously commented experiments of overall H$_2$S splitting in N$_2$, the UV photochemical H$_2$S splitting was also carried out in other mixtures simulating compositions of effluents in where H$_2$S 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$_2$S. The purpose is to show that the overall H$_2$S 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,

![Graph showing H$_2$S and H$_2$ concentration over time](image)

Figure 1. H$_2$ (solid lines) and H$_2$S (dashed lines) evolution at (top) 9.5 vol.% (black) and (bottom) 3.6 vol.% (red) and 1.5 vol.% (blue) initial H$_2$S 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>
<thead>
<tr>
<th></th>
<th>Gas composition before reaction (Vol.%)</th>
<th>Time (h)</th>
<th>Gas composition after reaction (Vol.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$_2$S</td>
<td>CH$_4$</td>
<td>CO$_2$</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>0</td>
<td>66</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>66</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>9.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>3.6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>1.5</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
the H₂S decomposition process could be applicable in most of the real gases without the need of H₂S purification. The results are summarized in Table 1. As can be seen in Table 1, the presence of CH₄ and CO₂ in large concentrations respect to H₂S, corresponding to compositions of real mixtures, does not interfere in the overall H₂S splitting, regardless H₂S concentrations (from 2 to 6 %), achieving complete removal of H₂S in few hours under our irradiation conditions, H₂S exhibiting the same photochemical behavior as in the absence of these gases. The time required for complete H₂S removal increases along its initial concentration. This is understandable considering that neither CH₄ nor CO₂ 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 H₂S splitting in the photochemical reaction in the presence of other gases can be easily explained considering the absorption spectra of CH₄ and CO₂. It has been widely reported that CO₂ do not absorb light at wavelengths larger than 200 nm[5], while CH₄ and N₂ are transparent and do not absorb UV light at all. In contrast, H₂S has an absorption from 270 nm into the deep UV. Fig. 2 presents the UV absorption spectrum of H₂S 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 H₂S aggregation at this concentration even in the gas phase.

Considering the UV absorption spectrum of H₂S shown in Fig. 2, the overall H₂S splitting was also tested at longer wavelengths. Specifically, the photochemical H₂S splitting was carried out at 300 nm and 354 nm. A mixture of 10.8 vol.% of H₂S in N₂ was used in this study, monitoring the H₂ evolution and H₂S disappearance as depicted in Fig. 3.

As can be observed in Fig. 3, H₂S irradiation at 300 or 354 nm did not allow the detection of measurable H₂ amounts. These negative results contrast with those observed upon 254 nm irradiation, where H₂ evolution occurs. This dependence of the irradiation wavelength on the photochemical overall H₂S splitting can be easily rationalized based on the UV absorption spectrum of H₂S shown in Fig. 2 that does not present significant photon absorption beyond 270 nm.

The quantum yield for light-induced H₂ generation was calculated by dividing the moles of H₂ formed per photons absorbed by H₂S for mixtures of 9.5 vol.% H₂S in N₂ upon 254 nm irradiation. By determining the lamp flux using a calibrated photodiode, it was found that 0.53 H₂ molecules were produced per photon absorbed when UV irradiation at 254 nm was used, and only 0.016 and 2.6·10⁻⁵ 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 H₂ 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 H₂S [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 H₂ from H· would require, then, another photon, either by splitting H-S· or by reaction of H· with photoexcited H₂S, 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 (6.1·10¹⁵ photons·s⁻¹), assuming a cost of 0.1 €×kWh⁻¹ gives a value of 0.01 g×€⁻¹ for H₂ 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](image2.png)

**Figure 2.** Gas-phase UV spectrum of 9.5 vol.% of H₂S in N₂.

![Figure 3](image3.png)

**Figure 3.** Temporal profiles of H₂ generation (solid lines) and H₂S disappearance (dashed lines) in mixtures containing an initial 10.8 vol.% H₂S 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 H₂ 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 H2S 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-dicyclohexyl disulfane (see structures in Scheme 1). Specifically, no evidence of the presence of cyclohexene thirane or cyclohexanethiol was observed. Although less informative, the transient absorption spectrum study was also carried out in aqueous solution by irradiating 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 H2S in aqueous solution and assigned to HS2 species.[11] Further evidence for this assignment was obtained here by measuring the steady-state absorption spectrum of Na2S2 in aqueous solution that is a stable disulfide commercially available. A band at 380 nm was recorded for Na2S2. Therefore, we can assume that the transient absorption signal found in the present case correspond to S22- 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.

![Scheme 1. Proposed mechanism for the overall H2S splitting upon 254 nm light irradiation showing the need of two photons for the generation of each H2 molecule and structures of the S-cyclohexene adducts observed in the quenching study.](image)

Figure 4. Transient absorption spectra of Na2S in aqueous solution (pH 7 – 8) upon 266 nm laser excitation at different times.

Conclusions

The photochemical H2S 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 H2 and S in quantitative yields. This process exhibits high quantum yield for H2 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 biodigesters, 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 N2 and H2S 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 °C 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 CS2 and the solution was analyzed by gas chromatography in a Varian 3900 apparatus equipped with a TRB-5MS column (5% phenyl, 95% polydimethylsiloxane, 30 m x 0.25 mm x 0.25 μm, Teknokroma), whereby sulphur was quantified to be formed in stoichiometric amounts respect the initial H2S 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.

Acknowledgements

Financial support by the Spanish Ministry of Economy and R1) and Generalitat Valenciana (Prometeo 2013-014) is gratefully acknowledged. Thanks are due to Dr. J.A. Agulló-Maciá for performing a preliminary experiment.

Keywords: photochemistry • H₂S • overall splitting • UV light • H₂ production

Overall $\text{H}_2\text{S}$ splitting in the absence of $\text{O}_2$ has been demonstrated upon 254 nm irradiation in the gas phase with 50% quantum yield.