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H₂S mediated thermal and photochemical methane activation

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Abstract

Sustainable, low temperature methods of natural gas activation are critical in addressing current and foreseeable energy and hydrocarbon feedstock needs. Large portions of natural gas resources are still too expensive to process due to their high content of hydrogen sulfide gas (H₂S) in mixture with methane, CH₄, altogether deemed as sub-quality or “sour” gas. We propose a unique method for activating this “sour” gas to form a mixture of sulfur-containing hydrocarbon intermediates, CH₃SH and CH₃SCH₃, and an energy carrier, such as H₂. For this purpose, we computationally investigated H₂S mediated methane activation to form a reactive CH₃SH species via direct photolysis of sub-quality natural gas. Photoexcitation of hydrogen sulfide in the CH₄+H₂S complex results in a barrier-less relaxation via a conical intersection to form a ground state CH₃SH+H₂ complex. The resulting CH₃SH can further be heterogeneously coupled over acidic catalysts to form higher hydrocarbons while the H₂ can be used as a fuel. This process is very different from a conventional thermal or radical-based processes and can be driven photolytically at low temperatures, with enhanced controllability over the process conditions currently used in industrial oxidative natural gas activation. Finally, the proposed process is CO₂ neutral, as opposed to the currently industrially used methane steam reforming (SMR).

Keywords

methane; H₂S; CH₃SH; C-H bond activation; DFT; light

Introduction

Natural gas is an economical alternative to petroleum that, due to its increased availability in the recent years, can act as a bridge into other, sustainable and renewable fuel or chemical sources.^[1] Largely composed of methane, natural gas production is steadily increasing due to the new, previously inaccessible unconventional sources, such as methane hydrates or shale gas.^[2, 3] While production technology^[4] and environmental^[5] issues still plague unconventional methane source usage, a mature technology of natural gas extraction and processing – methane oxidative coupling, partial oxidation, carbonylation - has been around for many decades.^[6] An outstanding issue with the natural gas, however, is its quality due to

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the presence of H₂S. Hydrogen sulfide concentrations in natural gas can range from a few ppm to still recoverable 5–7%^[7, 8] up to virtually unusable 90% by volume.^[9] The latter is called sub-quality natural gas (SQNG) and comprises, for example, approximately 30% of US natural gas resources^[10] with most of these SQNG wells capped and not utilized.^[11] Even small amounts of H₂S in natural gas put stringent criteria on the pipeline materials due to corrosion, while also poisoning heterogeneous catalysts during the steam methane reforming (SMR) reaction and hence need to be removed. The predominant industrial method for removing H₂S from natural gas currently proceeds via a combination of amine absorbent and the Claus process to yield elemental sulfur and H₂O^[12]

This, effectively, means that all of the hydrogen atoms are converted into water, an obvious waste of a precious energy carrier. Other methods that would recover hydrogen from H₂S have been developed via thermal, thermochemical, electrochemical, plasmachemical and photochemical treatments.^[13] Most of these require, however, methane-H₂S gas mixture separation before processing with the above mentioned methods and have intensive energy and instrumentation requirements. The one current method that doesn't call for the SQNG mixture separation is hydrogen sulfide methane reforming (HSMR) which conceptually is similar to SMR^[11]

HSMR is a highly endothermic process that proceeds at temperatures higher than 1000°C, above those typical for autothermal CH₄ decomposition. This renders HSMR very susceptible to coking which puts an upper limit to the temperature of the simultaneous CH₄ and H₂S reactions. The attractiveness of the HSMR process, however, is clearly no CO₂ byproduct generation, whereas SMR generated CO eventually yields CO₂.

Hydrogen formed via (3) and (4) can further be converted into liquid chemicals or fuels via the Fischer-Tropsch process. Alternative industrial routes of commodity chemical production are methanol-to-higher hydrocarbons – olefins (MTO), gasoline (MTG) - coupling.^[6] Methanol – CH₃OH – can be considered an activated, heterosubstituted form of methane^[14] that further reacts to produce higher hydrocarbons via heterogeneously catalyzed reactions, typically in acidic zeolites, such as H-ZSM-5 or nanoporous zeotype materials, such as H-SAPO-34.^[15] This reaction typically involves CH₃OH coupling into dimethyl ether, CH₃OCH₃, followed by ethylene formation with concomitant hydrocarbon chain growth depending on the experimental conditions^[16]

Further, other activated forms of CH₄, especially those involving halogens, such as CH₃Cl^[17] and CH₃Br,^[18] have been successfully coupled to produce higher hydrocarbons

on similar catalysts. With the earlier HSMR similarity to SMR drawn, CH₃SH, which is isostructural with CH₃OH, can also be considered a heterosubstituted form of CH₄. Olah *et al.* proposed that CH₃SH can also be coupled into olefins demonstrating that its coupled intermediate, CH₃SCH₃, over alumina supported WO₃ yields 63.8 % CH₄, 15.4 % C₂H₄, 18.5 % C₃H₆ with traces of other C₂, C₃ and C₄ compounds.^[14] Presumably, two major compounds present in SQNG, CH₄ and H₂S, can be converted into hydrocarbons via a reactive CH₃SH intermediate. The proposed reaction would involve not complete but partial H₂S decomposition into HS and H with the former activating CH₄ and the latter forming molecular hydrogen.

CH₃SH, as well as any resulting CH₃SCH₃, could then be proposed to be coupled in zeolitic type of heterogeneous catalysts to yield higher hydrocarbons via (8) and (9)

A true challenge here is the reaction (7) for which to our best knowledge no known catalyst exists. CH₃SH has previously been synthesized via CS₂ reaction with COS on K promoted Mo/SiO₂ catalysts or thiolation of CH₃OH,^[19, 20] but not directly from a mixture of CH₄ and H₂S.

As a first step, we explored the feasibility of the reaction (7) in the gas phase by employing quantum chemical calculations. We divided our approach between thermal and photolytic (radical) methods.^[21] In particular, we recognize the fact that CH₄ photodissociation proceeds when excited by light with a wavelength of 140 nm.^[22] This is a considerable amount of energy. Instead, we investigated H₂S, already present in the reaction mixture, as the source of reactive intermediates. This is based on a recently investigated phenomenon of neutral biradical formation from H₂S when irradiated with ~200 nm light.^[21] In the work below we attempt to combine conventional high temperature gas transformations with photochemically induced radical stimulated reactions to identify possible pathways of CH₃SH formation from SQNG without any prior separation or purification.

Theoretical methods

The long range corrected CAM-B3LYP density functional^[23] combined with the 6-311+G(2df,2p) basis set and integration grids containing 99 radial points in the Euler-MacLaurin quadrature grid and 590 angular points in the Lebedev grid was used for all ground (S0) and first excited (S1) state optimizations and frequency calculations. Accurate coupled cluster single point energies were determined at the CR-CC(2,3)^[24, 25] level of theory for the S0 states and the CR-EOMCC(2,3)^[24, 26, 27] level of theory for the S1 states, using the same basis set. The CR-CCL(2,3) level is also known as the CR-CCSD(T)_L level, while CR-EOML(2,3) is synonymous with CR-EOMCCSD(T)_L. Minima and transition states were confirmed by zero and one imaginary vibrational frequency, respectively. Enthalpy and free energy corrections were obtained at the CAM-B3LYP/6-311+G(2df,2p) level within the temperature range from 300 to 1600 K. Intrinsic reaction coordinate (IRC) calculations were performed to verify transition state geometry.^[28] All reaction energy diagrams are constructed using enthalpy or Gibbs free energy corrected CR-CC(2,3) or CR-EOMCC(2,3) energies. The ROHF treatment was applied when calculating ground state doublet radicals.

All density functional and coupled cluster calculations utilized the 1 May 2012 (R2) release of the GAMESS program suite^[29]. All second-order Moeller-Plesset (MP2) calculations were performed using the TURBOMOLE v6.3.1 package.^[30, 31] The resolution of identity (RI) approximation was used in combination with an augmented correlation consistent triple zeta basis set (aug-cc-pVTZ) on all atoms together with the corresponding auxiliary basis set.^[32]

Given that single-reference methods may fail for hemolytic processes and for probing the existence of a conical intersection on the potential energy surface, a complete active space self-consistent-field CASSCF wave function was constructed with an active space that contained 6 electrons and 5 orbitals from the valence space as detailed later in the text in Figure 4. Subsequently, complete active space second-order perturbation theory CASPT2 was used. In this approximation the CASSCF wave function is taken as a zeroth-order wave function and the remaining electron correlation effects are estimated by the second-order perturbation theory. The same basis set as in DFT calculations - 6-311+G(2df,2p) – was used. All multi reference calculations are performed with MOLCAS version 7.8.^[33]

Results and Discussion

Thermal and photochemical CH₄ activation with H₂S

Gas phase studies have been used in this work to study fundamental aspects of CH₄ activation at the molecular level. Kretschmer, Schlangen and Schwartz used very recently a similar approach to elucidate the role of transition metal electronic configuration on C-H bond perturbation in CH₄.^[34] Typical gas phase CH₄ activators used are metal clusters^[35–37] and their various ligated counterparts.^[38] Due to the recognized inherent stability of the tetrahedral CH₄ molecule, reactive solid state radical-containing metal oxide clusters have been utilized to yield C-H bond homolysis.^[38] Doublet ground state (D0) [Al₈O₁₂]⁺ clusters have been shown to possess spin localized on a sole oxygen atom and be very reactive towards hydrogen transfer reaction from CH₄.^[39] Conceptually, this would describe a feasible state-of-the-art method of gas phase CH₄ activation – the presence of a localized spin in the vicinity – but is very difficult to obtain since gas phase metal clusters cannot be applied on a large scale. On the other hand, H₂S has already been shown to produce a neutral biradical in the gas phase via photolysis at room temperature via sulfur p_z lone pair excitation into the symmetric S-H σ* molecular orbital.^[21] The excitation energy (~205 nm calculated using time dependent DFT and CAM-B3LYP/6-311+G(2df,2p)) is smaller than that of CH₄ electronic transition (~140 nm) which results in a CH₄ molecule photodissociation into methyl and hydrogen radicals as the first step.^[22] By analogy with the unpaired spin localized metal oxide nanoclusters described recently to activate the C-H bond in methane, H₂S in the presence of light can provide the same activating capability without a complicated catalyst preparation.

With this in mind, we elucidated electronic transitions of a hypothetical 1:1 CH₄:H₂S mixture on the electronic ground state (S0) and first excited state (S1) potential energy surfaces. A stable minimum of the CH₄+H₂S molecular complex found to have no imaginary frequencies on the CAM-B3LYP/6-311+G(2df,2p) S0 surface is shown in Figure 1. It has the form HSH...CH₄ with a corresponding H...S intermolecular distance of 2.95 Å. Weak intermolecular interactions are not well described using density functional theory and even though we used a long range corrected version of the B3LYP functional – CAM-B3LYP – we verified this bonding configuration between CH₄ and H₂S using correlated wave function methods and extensively augmented basis sets. MP2/aug-cc-pVTZ optimization reproduced the CH₄+H₂S bonding configuration with a HSH...CH₄ intermolecular distance of 2.71 Å. The intermolecular HSH...CH₄ distance is ~0.2 Å longer in the MP2/aug-cc-pVTZ optimized geometry than in the CAM-B3LYP/6-311+G(2df, 2p)

geometry, consistent with the higher level of theory. Slightly different intermolecular distance aside, as the MP2/aug-cc-pVTZ optimization verified the CAM-B3LYP/6-311+G(2df, 2p) minimum geometry, this is the only initial complex further used to explore thermal and photochemical reactions in CH₄ activation with H₂S.

Time dependent DFT calculations were performed at the CAM-B3LYP/6-311+G(2df, 2p) geometries with the same basis set to obtain excitations in the CH₄+H₂S molecular complex. It can be seen in Table 1 that the lowest energy excitation of ~205 nm is due primarily to intramolecular excitation (S p_z to S-H σ*) and is localized on the H₂S molecule. There is a small coupling also apparent, however, in MO 17 and MO 18 with the C-H bonds in methane. This transition also a small, but non-zero oscillator strength of 0.004. Further, the second lowest energy excitation of ~201 nm with the strongest oscillator strength (0.070) involves excitation also from the S p_z lone pair, but now into orbitals with significant density on methane. Thus, photoexcitation would result in weakening of the S-H bond and a possible charge transfer between the two molecular species.

To further investigate relative energetics of the molecular complexes involved in the possible CH₄+H₂S to CH₃SH+H₂ transformations, relative enthalpy and entropy values were calculated for the species involved on the S0 and S1 potential energy surfaces. CR-CC(2,3)/6-311+G(2df,2p)//CAM-B3LYP/6-311+G(2df,2p) calculated relative enthalpies at 300 and 1600 K are shown in Figure 2. A weak endothermic interaction between CH₄ and H₂S exists on the S0 surface with respect to the isolated CH₄ and H₂S at 0.99 and 6.14 kcal/mol for 300 and 1600 K, respectively. Products on the S0 surface, CH₃SH+H₂, are higher in energy than the interacting reactants by 16.52 and 18.50 kcal/mol for 300 and 1600 K, respectively. There is, however, a large kinetic barrier with the S0 transition state located at 107.37 and 111.82 kcal/mol for 300 and 1600 K, respectively. The calculated value is close to that of C-H bond dissociation enthalpy (104.99 kcal/mol and 298 K).^[40] Alternatively, stationary points on the S1 surface were located for both reactant and product minima but not for the transition state (TS). The initial excitation of the S0 optimized CH₄+H₂S complex requires 139.47 kcal/mol or 205 nm, a much smaller energy than that required for excitation of CH₄ alone. Optimized excited state complex lies ~30 kcal/mol lower with an asymmetry in S-H bond lengths of 1.34 and 1.94 Å. This signifies neutral biradical formation^[21] with the CH₄ geometry remaining unperturbed and the SH...C interatomic distance decreasing to 2.82 Å in the S1 state from 2.95 Å in the S0 state. This result is fully consistent with that predicted from the vertical excitation data – namely, the S-H bond is weakened while there is increased interaction between the two molecular moieties. The S1 state product lies about 12 kcal/mol higher than the optimized reactant. Ultimately, the excited state TS can be envisioned as the infinitely separated CH₃•, HS• radicals and H₂ molecule, all in the ground state. The sum of their energies was found to be 87.71 kcal/mol above reactants at 300 K suggest that a radical mechanism, either via photochemical or thermal excitation, would have much a lower energy of activation than the heterolytic S0 process. Notably, the S1 optimized reactant complex energy at 300 K is very close to that of the S0 TS, suggesting that the two could interconvert via a conical intersection.

The formation of CH₃SH+H₂ as final products on both the S0 and S1 PES has been investigated and the results are shown in Figure 3. On the S0 surface, increasing the temperature has an adverse effect on both the rate and spontaneity of the reaction. The Gibbs free energy of activation increases from 117.16 kcal/mol at 300 K to 155.29 kcal/mol at 1600 K. The formation of CH₃SH + H₂ also becomes less spontaneous as the temperature rises, being exergonic by 23.52 kcal/mol at 300 K, but exergonic by 41.53 kcal/mol at 1600 K. However, there is a notable trend towards exergonicity is the final products are taken to be methyl radical, HS radical and H₂, namely those products formed via homolysis of the C-S bond in CH₃SH. At 300 K, the radical products lie 79.55 kcal/mol above reactants, but

only 38.37 kcal/mol above reactants at 1600 K. In fact, our data suggest that at temperatures above ~1500 K, any CH₃SH formed will thermally homolyze to radical products.

The temperature dependence of both the relative enthalpies (Figure 2) and relative Gibbs free energies (Figure 3) can be understood when considering the change in entropy associated with each step of the proposed mechanism. For the majority of the reaction steps, a modest decrease in entropy is observed. Thus, as the temperature is increased, the relative Gibbs free energies increase by a small amount. The notable exceptions are the formation of CH₄ + H₂S TS and the direct formation of the CH₃ radical, HS• radical and H₂ gas, both on the S0 surfaces. For the former process, the decrease in entropy is significant and the TΔS term becomes large and negative as temperature increases, resulting in a much higher Gibbs free energy of activation at 1600 K than at 300 K. The converse is true for the direct dissociation reaction, where the entropy increases significantly, resulting in a much lower relative Gibbs free energy for the products at 1600 K than at 300 K.

There are two implications to these observations. First, the thermal pathway becomes increasingly disfavored as the temperature is raised due to the significant loss of entropy in the CH₄ + H₂S TS. Second, the nature of the favored product changes as the temperature is increased. At lower temperatures, CH₃SH + H₂ are the favored products. However, as the temperature increases, it is predicted that CH₃SH will cleave, leaving the CH₃ + SH radical pair as the final products, along with H₂. Our data indicate that the switchover occurs at ~1500 K.

The similar relative energies of the optimized S1 reactant complex to the S0 TS suggest that a conical intersection or seam may connect the S0 and S1 surfaces during the first half of the proposed reaction mechanism. Due to the biradical nature of the molecular system, the multireference CASPT2 method was applied to accurately estimate the energetics using the 6-311+G(2df,2p) basis set on the DFT optimized geometries. Figure 4 shows the active orbitals at the different geometries along the reaction path and Table 3 reports the occupation numbers of the active orbitals for the species on the S1 surface. In addition, the occupation of the active orbitals for the S0 state at the conical intersection is shown. The vertical excitation of the CH₄+H₂S complex transfers an electron from the non-bonding S-3p orbital to an approximately symmetric S-H σ* orbital. The contribution of the CH₄ moiety is negligible. When the geometry of the CH₄+H₂S complex is optimized on the S1 surface, the character of the S1 state does not undergo large changes. The unpaired electrons remain localized on the H₂S unit, albeit the singly occupied S-H σ* orbital is no longer symmetric involving both S-H bonds, but localized along the longer S-H bond. Profound changes are observed when the S1 state is analyzed in the geometry of the TS on the S0 surface. One of the singly occupied orbitals is now localized on the CH₃...H₂ unit and the other unpaired electron occupies the non-bonding S-3p orbital. This means that S1 has biradical character with spatially separated unpaired electrons, contrary to the previous case of CH₄+H₂S complex where the unpaired electrons were essentially localized on the same atom. This biradical character is also recognized in the S1 state at the conical intersection. One electron is in the S-3p_x orbital perpendicular to the HS...CH₃ bond (taking this bond as z-axis) and the other, mainly localized on CH₃, is in an orbital that is directed along this bond. The S0 state has exactly the same electronic character with the only difference that the unpaired electron on S is in the S-3p_y orbital. The S-3p(x,y) orbitals only weakly interact with the CH₃ and H₂ units and hence are nearly degenerate. This explains the fact that S0 and S1 are degenerate at this geometry. The electronic character of the S1 state is again rather similar for the S1 and S0 optimized geometry of the CH₃SH+H₂ complex. In both cases the two unpaired electrons are localized in a mainly non-bonding S-3p orbital and a S-H σ* orbital.

The CASPT2 estimate of the vertical excitation energy in the $\text{CH}_4+\text{H}_2\text{S}$ complex of 143.02 kcal/mol (200 nm) is in excellent agreement with values from TD-DFT calculations and experimental data from the isolated H_2S molecule.^[21] The geometry optimization on the S1 surface lowers the S1 energy by approximately 40 kcal/mol and puts the system very close in energy to the conical intersection, less than 3 kcal/mol above the minimum. An approximate minimum energy pathway (MEP) between the conical intersection and other stationary points located using the CAM-B3LYP/6-311+G(2df,2p) geometries was calculated using CASTP2/6-311+G(2df,2p) and is shown in Figure 5 together with the corresponding conical intersection geometry. This MEP was constructed as an interpolation between the stationary points on the PES with no gradient correction and thus the MEP points as cannot be considered to be stationary points on the PES. It can be seen that the S0 CASPT2 energy continuously lowers along a linear interpolation from the conical intersection to the $\text{CH}_3\text{SH}+\text{H}_2$ minimum on the S0 surface. Importantly, there is also a downhill path from the $\text{CH}_4+\text{H}_2\text{S}$ S0 geometry to the conical intersection on the S1 surface. Hence, immediately after the vertical excitation of the initial complex, the system can evolve on the S1 surface to the conical intersection by the simultaneous breaking of the C-H bond and formation of the H_2 unit. The bond breaking of the S-H bond is rather favorable on the S1 surface due to the occupancy of the anti-bonding sigma S-H orbital in this electronic state. On the other hand, if the system first evolves to the geometric minimum of the $\text{CH}_4+\text{H}_2\text{S}$ complex on the S1 surface, it has to overcome a barrier to reach the conical intersection, and hence, this pathway is less probable. The approximate MEP scan from $\text{CH}_4+\text{H}_2\text{S}$ (S1) to the conical intersection shows a shallow minimum, where S0 and S1 have virtually the same energy. This suggests that the CASPT2 conical intersection does not exactly coincide with the estimate of this stationary point based on CAM-B3LYP calculations. This is, of course, not unexpected; different computational methods can give different stationary points. However, both the relative energy and the geometrical parameters are rather similar. The largest difference lies in the distance of the H_2 unit to the $\text{CH}_3\cdots\text{SH}$ complex, which is determined by a rather weak interaction. The resulting flat potential energy surface easily gives rise to small differences in the H_2 to $\text{CH}_3\cdots\text{SH}$ distance. Note that the exact geometry of the CASPT2 conical intersection (or any of the other CASPT2 stationary points) has not been determined.

An important observation emerges where the $\text{CH}_4+\text{H}_2\text{S}$ molecular complex can be excited by ~200 nm light and relax directly to $\text{CH}_3\text{SH}+\text{H}_2$ S0 product via a barrier-less conical intersection. This effectively can help to circumvent the large thermal activation barrier and endergonicity, both of which increase with an increase in temperature, as shown in Figure 3. The relative contributions of the two competing pathways after the initial $\text{CH}_4+\text{H}_2\text{S}$ molecular complex excitation – via S1 optimized $\text{CH}_4+\text{H}_2\text{S}$ complex with the most probable HS^*+H^* radical pair formation and relaxation via conical intersection into $\text{CH}_3\text{SH}+\text{H}_2$ – can be proposed to be controlled via pressure. High pressures would favor associative processes,^[41] hence relaxation via the conical intersection, as opposed to the dissociative radical pathway which would be favored at lower pressures.

CH_4 activation with H_2S via radical reactions

Single reference methods, such as DFT, fail to reproduce accurate potential curves for homolytic cleavage of bonding electron pairs into infinitely-separated radical pairs. Thus, H_2S optimized on the S1 surface is still bound with a $\text{HS}\cdots\text{H}$ distance of 1.94 Å (Figure 2). In contrast, CASPT2 optimization of S1 H_2S shows complete S-H bond dissociation. It is therefore reasonable to assume that photoexcitation of the reactant complex will lead to formation of at least some radical species. Furthermore, a clear shift towards lower endergonicity for formation of infinitely separated $\text{CH}_3(\text{D}0)$, $\text{HS}(\text{D}0)$ and $\text{H}_2(\text{S}0)$ species (Figure 3) demonstrates that these radical species are expected at higher temperatures and

lower pressures. Finally, photolysis of H₂S molecules with 228 nm UV radiation was reported to produce “hot” reactive hydrogen radicals via reaction (11) with a substantial translational energy capable of driving further hydrogen abstraction reactions.^[42, 43] In the absence of hydrogen radical scavengers, hydrogen abstraction from CH₄ can proceed, resulting in effective CH₄ activation. The net result is that photolysis at elevated temperatures and reduced pressures should cause radical mechanisms to dominate over the S0 mechanism presented in Figure 3.

At low pressures, if the conical intersection mechanism is bypassed, numerous radical chain reactions become possible. The Claus process has been shown to include 150 radical based reactions,^[44] and only a small subset is investigated here. The calculated thermodynamic parameters at various temperatures for the following reactions are shown in Figures 6 and 7. In particular, initiation would proceed via (10) and (11)

H₂S photolysis has been shown to be very efficient with measured quantum yield close to unity.^[45] It has been reported that radiation <200 nm can yield elemental sulfur whereas >200 nm the primary products are H[•] + HS[•].^[46] At these wavelengths, CH₄ activation would not proceed efficiently as 140 nm excitation is necessary.^[22] Consecutively, propagation reactions would mostly involve HS[•] and H[•] radicals with contribution from CH₃[•] available only at later propagation stages. From Figures 6 and 7 it can be seen that the initiation steps become increasingly more favorable with increasing temperature, due to the increase in entropy, but never become exergonic even at 1600 K making thermal initiation impractical. While thermal radical initiation via (10) and (11) cannot be achieved, low pressure light or plasma excitation at 205 nm would ensure the feasibility of this rate limiting step at any given temperature.

Propagation would involve a set of reactions (12) through (20) where HS[•] and H[•] radicals play a predominant role while CH₃[•] would be also available

While there is very little temperature dependence on the thermochemical parameters of the radical propagation reactions investigated as shown in Figure 6, it is apparent that two subsets of reactions can be identified as endergonic and exergonic nature. This is in agreement with dielectric-barrier discharge reactor activated $\text{CH}_4 + \text{CO}_2$ experiments where low temperatures (300 K) were used to generate syngas.^[47] Methyl sulfide radical formation via reaction (18), together with $\text{HS}^\bullet$ propagation reactions (12) and (17) are all exergonic and exothermic, (18) and (17) in agreement with the literature values of -16.8 and -13.9 kcal/mol, respectively^[44]. Further, reaction (12) has been shown to proceed very fast without any CH_3SH generation.^[48] Propagation reactions (14) and (16), generating CH_3SH and $\text{CH}_3^\bullet$ respectively, can be viewed as rate limiting. It is also known that the photodissociation of CH_3SH , itself,^[21] requires less energy than that necessary to photodissociate H_2S . Photolytic products of CH_3SH at 254 (214) nm have indeed been reported to be H_2 with $\Phi=0.83$ (0.66), CH_4 with $\Phi=0.16$ (0.35) and CH_3SSCH_3 with $\Phi=0.99$ (1.03).^[49] In addition, propagation reaction (19) is favorable, suggesting that CH_3SH will also be depleted to form CH_3SCH_3 . Thus, it is expected that radical reactions would yield predominantly H_2 with some $\text{CH}_3\text{S}^\bullet$ based intermediates.

Radical termination reactions involve a set of reactions (21) through (26)

It can be seen that radical termination preferably proceeds via (23) and (24), e.g. preferentially forming H_2 and C_2H_6 . CH_3SH and CH_3SCH_3 forming reactions also proceed exergonic and exothermic but to a lesser extent whereas S-S bond formation is the least favored. These data show that the complex product mixture formed would predominantly consist of C_2H_6 and H_2 since C-S bond formation is not effective during the propagation step. C_2 hydrocarbon formation has indeed been shown to efficiently proceed in natural gas coupling via the cold plasma process.^[50, 51]

Collectively, these data show that low-pressure photolytic activation of $\text{CH}_4 + \text{H}_2\text{S}$ mixture would result in a radical chain reaction resulting in a distribution of products containing C_2 hydrocarbons, H_2 , CH_3SH and CH_3SCH_3 . The pure radical-driven process would need to operate on natural gas with higher H_2S concentrations to ensure a reasonable rate of

collisions in the propagation steps to maximize the rate of C-S bond formation. The resulting mixture can be separated since all S-C containing compounds have higher molecular weight and thus would have higher boiling points than C₂ hydrocarbons and H₂. The recovered CH₃SH and CH₃SCH₃ could be coupled into higher hydrocarbons heterogeneously, as they have been reported to undergo a facile transformation to yield C₂-C₄ hydrocarbons on WO₃ on Al₂O₃ via surface methoxy species.^[14] While the reactions considered might not represent the complete pool of radical reactions, they agree with the observed nonoxidative plasma catalytic CH₄ conversion data where up to 32% of C₂ hydrocarbons were produced with 15–40% of H₂ as byproduct.^[52]

A pronounced temperature dependence is noted for the change in Gibbs free energy for some reactions, but not for others (Figure 7). For the two initiation reactions (reactions 10 and 11), the change in entropy is large and positive, leading to a significant decrease in Gibbs free energy as the temperature increases. Exactly opposite is observed for the termination reactions (reactions 21 – 26). These results are expected as initiation increases the number of particles present while termination decreases the number of particles present. The temperature dependence of the propagation steps is modest, as the changes in entropy remain relatively constant over the range of temperatures probed. As the temperature increases, spontaneous thermal initiation becomes more likely, while termination becomes less likely and propagation is largely unaffected. Interestingly, the Gibbs free energy required for activation becomes similar to the Gibbs free energies of the least favorable propagation steps at the highest temperatures examined. This suggests that this radical cascade becomes feasible in the absence of photocatalysis only at temperatures in the vicinity of 1600 K, far too high for any practical application.

Conclusions and Implications

In this work, we unraveled fundamental thermal, photochemical and radical pathways towards CH₃SH formation from CH₄ and H₂S (direct hydrogen sulfide methane reforming). The work was motivated by the need for a conceptually novel approach of catalytically transforming SQNG to make it accessible in a sustainable and cost effective manner. This gas comprises about 30% of natural gas resources in the US^[10] and is currently deemed as inaccessible due to the high H₂S content and absence of cost effective technologies to deal with it. If formed directly from acidic natural gas, CH₃SH can then be coupled over acidic heterogeneous catalysts into higher hydrocarbons thus providing for a conceptually new MTG – *Mercaptan*-To-Gasoline- process. We argue here that the photochemical excitation of CH₄+H₂S mixture would result in CH₃SH+H₂ products at low temperatures and higher pressure via relaxation through a conical intersection. At very high temperatures or lower pressures via purely radical transformations, the CH₄+H₂S mixture could also transform into C₂ hydrocarbons, H₂ and several CH₃S• based species, such as CH₃SCH₃, which already can be considered as activated methane equivalents and can be relatively easily coupled over bifunctional heterogeneous catalysts.

High quantum yields of H₂S photolysis^[45] would mean practically achievable high yields. Furthermore, light induced transformations, as opposed to high temperature experiments, can be easily controlled by pulsing the light and providing an unprecedented control over the reaction products. For example, H₂S photolysis with a pulse of a few μs results in three times as large concentration of HS•, than that of 150 μs pulse.^[46] CH₃SH generation via non thermal pulsed plasma method has been patented, but the underlying mechanism only mentioned CH₃•, HS• and H• radical formation, e.g. the non-preferred radical pathway investigated here.^[53]

To decrease the large calculated thermal activation barriers, metal sulfide solid catalysts can be proposed, heuristically based on hydrodesulfurization active metals, such as Ru, W, Ni, Mo or Co. However, sulfur containing hydrodesulfurization reaction proceeds via thermodynamically favorable route to form H₂S and experimental conditions would need to be adjusted. Further, it must be noted that various forms of most of the proposed sulfide catalysts, such as CoS,^[54] RuS₂,^[55] NiS,^[56] MoS₂,^[57] WS₂,^[58] are low bandgap (1.1 to 1.8 eV) semiconductor materials thus absorbing most of the visible irradiation. This, in turn, presents an excellent opportunity of performing not only direct light induced homogeneous reactions, but also to explore photoexcited solid state generated charge carrier reactivity. It has already been shown that some sulfur resistant photocatalysts, such as FeGaO₃, can yield dissociated H₂S under visible light (λ 420 nm) in the presence of 1% NiO_x cocatalyst in aqueous solution.^[59] Gas phase photocatalytic water splitting has already been shown to proceed using visible light on Rh_{2-y}Cr_yO₃/GaN:ZnO.^[60] We propose that owing to the much lower heat of formation than that of H₂O, H₂S can also be decomposed in visible light on low bandgap semiconductor photocatalysts to further reform with CH₄. Computational studies of these processes are underway.

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Figure 1. CAM-B3LYP/6-311+G(2df, 2p) optimized stable minimum of CH₄+H₂S molecular complex. Relevant frontier MOs involved are shown at each geometry. Isosurface parameter is 0.03. Relevant properties are summarized in Table 1.

Figure 2.

CR-CC(2,3) - CR-EOMCC(2,3)/6-311+G(2df, 2p)//CAM-B3LYP/6-311+G(2df, 2p) reaction *enthalpy* (ΔH) diagram of direct S0 and S1 transformations of CH_4 and H_2S into CH_3SH and H_2 . All enthalpies are referenced to those of separated CH_4 and H_2S optimized in the S0 state and are shown in Table 2. No TS structure was located on S1 PES surface. Vertical excitation of $\text{CH}_4 + \text{H}_2\text{S}$ complex is shown in a dashed line. Arrows show increase or decrease of the calculated value when going from 300 to 1600 K. Sum relative enthalpies of separated CH_3^* (D0), SH^* (D0) and H_2 (S0) molecules are also shown.

Figure 3.

CR-CC(2,3) - CR-EOMCC(2,3)/6-311+G(2df, 2p)//CAM-B3LYP/6-311+G(2df, 2p) reaction *Gibbs free energy* (ΔG) diagram of direct S_0 and S_1 transformations of CH_4 and H_2S into CH_3SH and H_2 . All free energies are referenced to those of separated CH_4 and H_2S optimized in the S_0 state and are shown in Table 2. No TS structure was located on S_1 PES surface. Vertical excitation of the $\text{CH}_4 + \text{H}_2\text{S}$ complex is shown in a dashed line. Arrows show increase or decrease of the calculated value when going from 300 to 1600 K. Sum relative free energies of separated $\text{CH}_3^\bullet$ (D0), $\text{SH}^\bullet$ (D0) and H_2 (S_0) molecules are also shown.

Figure 4. CASPT2/6-311+G(2df, 2p)//CAM-B3LYP/6-311+G(2df, 2p) active space orbitals of (a) $\text{CH}_4+\text{H}_2\text{S}$ S0, (b) $\text{CH}_4+\text{H}_2\text{S}$ S1, (c) TS on the S0 surface (d) conical intersection, (e) $\text{CH}_3\text{SH}+\text{H}_2$ S1 and (f) $\text{CH}_3\text{SH}+\text{H}_2$ S0.

Figure 5.

Top: CASPT2/6-311+G(2df, 2p)//CAM-B3LYP/6-311+G(2df, 2p) reaction *electronic energy* (ΔE) diagram of direct S0 and S1 transformations of CH_4 and H_2S into CH_3SH and H_2 around the conical intersection. All CASPT2 energies are referenced to those of $\text{CH}_4+\text{H}_2\text{S}$ optimized in S0 and S1 state using DFT optimized geometries. Bottom: CASPT2/6-311+G(2df, 2p)//CAM-B3LYP/6-311+G(2df, 2p) calculated minimum energy path (MEP) diagram of direct S0 and S1 transformations of CH_4 and H_2S into CH_3SH and H_2 around the conical intersection. All stationary point CASPT2 energies are referenced to those of $\text{CH}_4+\text{H}_2\text{S}$ optimized in S0 and S1 state using DFT optimized geometries whereas point in MEP are linear interpolation with no gradient calculation.

Figure 6.

CR-CC(2,3)/6-311+G(2df, 2p)//CAM-B3LYP/6-311+G(2df, 2p) calculated enthalpies and Gibbs free energies of the free radical reactions 1 through 16 for the initiation, propagation and termination steps.

Figure 7. CR-CC(2,3)/6-311+G(2df, 2p)//CAM-B3LYP/6-311+G(2df, 2p) calculated $-T\Delta S$ term of the free radical reactions 1 through 16 for the initiation, propagation and termination steps.

Table 1CAM-B3LYP/6-311+G(2df,2p) S0 optimized CH₄+H₂S molecular complex properties.

Properties		CH ₄ +H ₂ S		
Lowdin population ^a	S1	16.25		
	H	0.86		
	C1	6.73		
Excitations	Lowest energy transitions involved	1	2	3
	Dominant contribution coefficients ^b	14->17 14->18	14->15 14->16	14->15 14->16 14->17 14->18 14->20
	Excitation energy, nm	205.1	200.4	160.6
	Oscillator strength, arb units	0.004	0.070	0.000

^aLowdin populations of the S1-H-C1 linkage.^bOnly contribution coefficients higher than 0.2 are shown.

Table 2

CAM-B3LYP/6-311+G(2df,2p) optimized CH₄ and H₂S reaction to form CH₃SH and H₂ S0 and S1 relative enthalpies and free energies.^a

Species	$E_{\text{CR-CC}(2,3)} (E_{\text{CR-EOMCCSD}}(\text{T})/6\text{-}311+\text{G}(2\text{df},2\text{p}), \text{Hartree})$	Enthalpy Corr. 300 K (1600K), kcal/ mol	Gibbs Corr. 300 K (1600K), kcal/ mol	$\Delta H_{300\text{K}, 1600\text{K}}$ $\Delta G_{300\text{K}, 1600\text{K}}$, kcal/mol
CH ₄	-40.432735	30.60 (50.98)	15.77 (-65.28)	-
H ₂ S	-398.925611	11.95 (25.48)	-3.22 (-81.69)	-
CH ₄ +H ₂ S S0	-439.358696	43.75 (82.82)	16.36 (-137.32)	0.99, 6.14 3.59, 9.43
CH ₄ +H ₂ S S1	-439.179119	40.59 (81.34)	14.74 (-134.23)	110.51, 117.34 114.66, 125.20
CH ₄ +H ₂ S S0 TS	-439.182135	39.34 (77.71)	19.14 (-102.25)	107.37, 111.82 117.16, 155.29
CH ₃ SH+H ₂ S1	-439.155070	41.38 (82.43)	17.40 (-124.11)	122.97, 131.91 128.57, 142.59
CH ₃ SH+H ₂ S0	-439.328592	37.96 (80.82)	37.96 (-131.94)	17.51, 24.64 23.52, 41.53

^a CR-CC(2,3)/6-311+G(2df,2p) or CR-EOMCCSD(T)/6-311+G(2df,2p) energy plus CAM-B3LYP/6-311+G(2df,2p) enthalpy (free energy) correction to 300 or 1600 K. Energies are referenced to sum of CH₄ S0 and H₂S S0 optimized at infinite separation.

Table 3

CASTP2/6-311+G(2df,2p)//CAM-B3LYP/6-311+G(2df,2p) calculated reactant, product and conical intersection natural orbital occupation numbers of S1. The occupation numbers for S0 in the conical intersection are given for comparison.

Species	Natural orbitals				
	1	2	3	4	5
CH ₄ +H ₂ S0	1.990	1.993	0.999	0.016	1.001
CH ₄ +H ₂ S1	1.998	1.989	1.000	1.000	0.013
TS0	1.999	1.974	0.999	1.001	0.027
Conical S0	1.978	0.999	1.999	1.001	0.023
Conical S1	1.978	1.999	0.998	1.002	0.023
CH ₃ SH+H ₂ S1	1.998	1.996	1.000	1.000	0.006
CH ₃ SH+H ₂ S0	1.996	1.998	1.008	0.005	0.992