First Detection of Interstellar S₂H

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Abstract

We present the first detection of gas-phase S₂H in the Horsehead, a moderately UV-irradiated nebula. This confirms the presence of doubly sulfurretted species in the interstellar medium and opens a new challenge for sulfur chemistry. The observed S₂H abundance is \( \sim 5 \times 10^{-11} \), only a factor of 4–6 lower than that of the widespread H₂S molecule. H₂S and S₂H are efficiently formed on the UV-irradiated icy grain mantles. We performed ice irradiation experiments to determine the H₂S and S₂H photodesorption yields. The obtained values are \( \sim 1.2 \times 10^{-3} \) and \( < 1 \times 10^{-5} \) molecules per incident photon for H₂S and S₂H, respectively. Our upper limit to the S₂H photodesorption yield suggests that photodesorption is not a competitive mechanism to release the S₂H molecules to the gas phase. Other desorption mechanisms such as chemical desorption, cosmic-ray desorption, and grain shattering can increase the gaseous S₂H abundance to some extent. Alternatively, S₂H can be formed via gas-phase reactions involving gaseous H₂S and the abundant ions S⁻ and SH⁻. The detection of S₂H in this nebula therefore could be the result of the coexistence of an active grain-surface chemistry and gaseous photochemistry.

Key words: astrochemistry – ISM: abundances – ISM: individual objects (Horsehead) – ISM: molecules – methods: laboratory: solid state – photon-dominated region (PDR)

1. Introduction

Sulfur is one of the most abundant elements in the universe \((S/H \sim 1.3 \times 10^{-5})\) and plays a crucial role in biological systems on Earth, so it is important to follow its chemical history in space. Surprisingly, sulfurretted molecules are not as abundant as expected in the interstellar medium. A few sulfur molecules have been detected in diffuse clouds demonstrating that the sulfur abundance in these low-density regions is close to the cosmic value (Neufeld et al. 2015). A moderate sulfur depletion (a factor of 4) is observed in the external layers of the photodissociation region (PDR) in the Horsehead nebula as well (Goicoechea et al. 2006). In cold molecular clouds, a large depletion of sulfur is usually considered to reproduce the observations (see, for instance, Tieftrunk et al. 1994). However, recent models by Vidal et al. (2017) explained the observational data without or with little sulfur depletion after updating the gas and grain chemistry. In that case, HS and H₂S on the grains or atomic sulfur in the gas would contain most of the sulfur. In hot cores and coronis, Wakelam et al. (2004) found that observations of S-bearing molecules would be better reproduced if sulfur was sublimated from grains in the atomic form or if it was quickly converted into it. Thus far, the main solid or gas sulfur carrier is still debated.

With an adsorption energy of \( \sim 1100 \) K (Hasegawa & Herbst 1993), sulfur atoms are expected to stick on the surfaces of grains with temperatures below \( \sim 22 \) K. Here, because of the high hydrogen abundances and the mobility of hydrogen in the ice matrix, sulfur atoms are expected to form H₂S. Indeed, gaseous H₂S is the most abundant S-bearing molecule in comets, with an abundance of up to 1.5% relative to water (Bockelée-Morvan et al. 2000). A firm detection of H₂S in interstellar ices has not been reported yet. A realistic upper limit of the H₂S abundance in interstellar ices is 1% relative to water that is 10 times lower than the cosmic abundance (Jiménez-Escobar & Muñoz Caro 2011). One possibility to explain the low fraction of H₂S in interstellar ices is that H₂S is processed by UV photons or cosmic rays in the ice leading to the formation of other S-bearing species. OCS and, tentatively, SO₂ have been detected in icy mantles but their abundances are far too low to explain the missing S budget (Geballe et al. 1985; Palumbo et al. 1995; Boogert et al. 1997).

Trying to provide new insights into the ice composition, experimental simulations of the irradiation of interstellar ices containing H₂S under astrophysically relevant conditions have been performed in laboratory using UV photons (Jiménez-Escobar & Muñoz Caro 2011; Jiménez-Escobar et al. 2014), X-rays (Jiménez-Escobar et al. 2012), or ions (Moore et al. 2007; Ferrante et al. 2008; Garozzo et al. 2010). Energetic processing of H₂S-bearing ices readily generates sulfur–sulfur bonds, and the main S-bearing products in these experiments are H₂S₂ and S₂H, which were detected by Jiménez-Escobar & Muñoz Caro (2011) through their infrared absorption bands. The molecule H₂S₂ could subsequently photodissociate, forming S₂ and S₃ depending on the irradiation time. These molecules with two S atoms and even more could thus contain...
a significant fraction of the missing sulfur in dense clouds. In line with this work, Druard & Wakelam (2012) suggested that polysulphanes could be a sulfur reservoir in the ice and are rapidly converted into atomic sulfur once in the gas phase. Martín-Doménech et al. (2016a) unsuccessfully searched for S2H and H2S2 in the gas phase toward the well-known hot corino, IRAS 16293–2422. The lack of gaseous S2H and H2S2 was interpreted as the consequence of the rapid destruction of these species once sublimated in such a warm and dense environment (Martín-Doménech et al. 2016a; Forbenerry & Francisco 2017).

In this Letter, we report the first interstellar detection of S2H in the prototypical PDR, the Horsehead. In Section 4, we discuss the possible grain-surface and gas-phase S2H formation routes. New measurements of the photodesorption yields of S2H and H2S are presented in Section 5.

2. Observations and Data Reduction

The data used in this work are from the Horsehead Wide-band High-resolution Iram-30 m Surveys at two Positions with Emir Receivers (WHISPER; PI: J. Pety) project and the Director’s Discretionary Time project D11-16. The Horsehead WHISPER project is a complete, unbiased line survey of the 3, 2, and 1 mm bands using the IRAM 30 m telescope. Two positions are observed: (i) the HCO peak (R.A. = 5°40′53″936, decl. = −2° 28′00″, J2000), which is characteristic of the PDR at the UV-illuminated surface of the Horsehead nebula (Gerin et al. 2009; also referred to as the PDR position), and (ii) the DCO+ peak (R.A. = 5°40′55″61, decl. = −2°27′38″, J2000), which corresponds to a cold and UV-shielded condensation located less than 40′ away from the PDR edge (Pety et al. 2007). During the observations we used the Position-Switching procedure with the reference position located at an offset (−100′, 0) relative to R.A. = 5°40′54″27, decl. = −02°28′00″. Several lines of S2H were tentatively detected toward the two positions observed in the WHISPER survey. In order to confirm the S2H detection, we requested Director’s Discretionary Time (D11-16) to observe a single setup covering the frequencies listed in Table 1. The merged S2H spectra are shown in Figure 1. Line intensities are given in main brightness temperature (TMB), and the lines were observed with a frequency resolution of 49 kHz.

In order to have a deeper insight into the S2H chemistry, we compare the new S2H observations with the H2S l1→l0 map observed during 2006 April with the IRAM 30 m telescope. These observations were done using the frequency-switching mode and a spectral resolution of 40 kHz. The averaged noise level per resolution element at 168 GHz is rms(TMB) = 170 mK. The integrated intensity emission of the H2S line varies between 1.0 and 1.5 K km s−1 across the molecular cloud with an abrupt border in the west (see Figure 1). The H2S emission presents a local minimum toward the DCO+ peak, similar to the morphology observed in other species such as CH3OH (Guzmán et al. 2011, 2013), suggesting gaseous H2S depletion toward this cold dense core.

3. Column Densities and Abundances

The rotational spectrum of S2H was calculated by Tanimoto et al. (2000). The spectroscopic data can be found in the CDMS catalog (Müller et al. 2005). We have detected eight S2H lines located at 94526.1508, 94526.3208, 94731.0115, 94731.2080, 94972.1104, 110294.0282, 110294.1530, 110497.9666, and 110498.1104 MHz. The S2H hyperfine transitions are forming doublets very close in frequency (~0.12 MHz) that remain unresolved in our data (see Figure 1). In Table 1, we show the Gaussian fits to the observed line features, each one clearly detected with S/N > 5. We have adopted as the central frequency the most intense component of the doublet. For this reason the central velocity shown in Table 1 is systematically shifted by ~0.2–0.5 km s−1 from the Horsehead systemic velocity, 10.5 km s−1. We have checked possible contamination by other compounds using the CDMS and JPL catalogs. There is no other good candidate to be a carrier of these lines. The large line width of the 94.731 GHz line toward the DCO+ peak position, ~1.7 km s−1, is more likely due to the poor baseline around this feature.

The WEEDS software has been used to simulate the S2H spectrum in the whole frequency coverage of the WHISPER survey assuming LTE conditions. We have fitted the detections and upper limits of 97 lines with upper level energies lower than 75 K found in the frequency range of the full survey using the Bayesian method described by Majumdar et al. (2017). The whole spectrum can be fitted assuming that the emission uniformly fills the beam and the rotation temperatures and S2H column densities listed in Table 2. The fitted line widths are 0.68 ± 0.12 km s−1 for the core and 0.63 ± 0.1 km s−1 for the PDR. The observed S2H line widths are consistent with the emission coming from the UV-irradiated gas. Species that are more abundant in the cold and UV-shielded gas of the core as DCO+ and H13CO+ present narrower line widths toward the DCO+ peak than toward the PDR (Goicoechea et al. 2009). However, others PDR-like species such as HCO present similar line widths toward both positions (Gerin et al. 2009). This suggests that even toward the core position, the S2H emission is
mainly coming from the UV-illuminated layers of the cloud along the line of sight.

The \( \text{S}_2\text{H} \) rotation temperatures reveal subthermal excitation and are similar to those derived for other high dipole moment compounds like \( \text{o-H}_2\text{CO} \) (Guzmán et al. 2011). The estimated abundance (w.r.t. hydrogen nuclei) is \( \sim 5 \times 10^{-11} \) toward the DCO\(^+\) peak and about a factor of 2 larger toward the HCO peak.

From a chemical point of view, it is interesting to compare the \( \text{S}_2\text{H} \) abundance with those of the related species \( \text{H}_2\text{S} \).

Unfortunately, the only observable transition with the 30 m telescope, given the physical conditions in the Horsehead, is \( \text{o-H}_2\text{S} \, ^{1}_{1,0} \rightarrow ^{1}_{0,1} \). Thus, we need to assume a rotation temperature to derive the \( \text{H}_2\text{S} \) column density. Since the \( \text{H}_2\text{S} \) dipole moment (\( \mu_b = 0.978 \text{ D} \); Viswanathan & Dyke 1984) is similar to those of \( \text{S}_2\text{H} \) (\( \mu_b \approx 1.16 \text{ D}, \mu_b \approx 0.827 \text{ D} \); Peterson et al. 2008), we assume the same rotation temperature for both molecules. With these assumptions and adopting an ortho-to-para ratio of 3, we derive a \( \text{H}_2\text{S} \) abundance of \( \sim 3 \times 10^{-10} \) toward the two positions. This would imply that \( [\text{S}_2\text{H}] / [\text{H}_2\text{S}] = 0.15 \pm 0.09 \) in the DCO\(^+\) peak and \( [\text{S}_2\text{H}] / [\text{H}_2\text{S}] = 0.27 \pm 0.14 \) toward the HCO peak. These numbers are consistent with the \( [\text{S}_2\text{H}] / [\text{H}_2\text{S}] \) ice ratio obtained by Jiménez-Escobar et al. (2013) in their simulations of UV irradiation of \( \text{H}_2\text{S} \) ices. In the following, we qualitatively explore the possible surface and gas-phase formation routes of \( \text{S}_2\text{H} \).

4. \( \text{S}_2\text{H} \) Formation

The formation of \( \text{S}_2\text{H} \) is an intricate problem due to the low H-SS energy bonding. Evidence for the formation of \( \text{S}_2\text{H} \) during irradiation of pure \( \text{H}_2\text{S} \) and \( \text{H}_2\text{S}:\text{H}_2\text{O} \) ice mixtures was provided by Jiménez-Escobar & Muñoz Caro (2011) using the same experimental setup as the one described here. One way of forming \( \text{S}_2\text{H} \) could be the grain-surface reactions: \( \text{s-H} \) atom (hereafter, “s-” is used to refer to the solid phase) addition on \( \text{s-S}_2 \), and \( \text{s-S} + \text{s-HS} \) reaction, followed by chemical desorption. However, the low exothermicity of the first reaction should prevent efficient chemical desorption (Minissale et al. 2016; Wakelam et al. 2017). The second reaction should not be efficient in cold cores because, below 15 K, S atom and HS radical are not mobile on ice considering the adsorption energies given by Wakelam et al. (2017). Moreover, \( \text{S}_2\text{H} \) is a very reactive species in the gas phase, reacting with H, N, C, and O atoms without a barrier, so likely also on surface. An alternative surface-induced \( \text{S}_2\text{H} \) production may be \( \text{s-H}_2\text{S}_2 \) photodissociation desorption: \( \text{s-H}_2\text{S}_2 + h\nu \rightarrow \text{s-S}_2 + \text{H}_2\text{S} \), but it needs mobile HS on ice and therefore a high grain temperature.

In the gas phase, \( \text{S}_2\text{H} \) may be produced by the electronic dissociative recombination of \( \text{H}_2\text{S}_2^+ \). Even if there is no data on this reaction, the loss of one H atom is always an important exit channel on dissociative recombination (Plessis et al. 2010). There are two known \( \text{H}_2\text{S}_2^+ \) production pathways: the \( \text{S}^+ + \text{H}_2\text{S} \rightarrow \text{H}_2\text{S}_2^+ + h\nu \) reaction (Anicich 2003), despite the fact that the reference is an unpublished work and previous experimental studies did not identify this channel (Smith et al. 1981), and the \( \text{SH}^+ + \text{H}_2\text{S} \rightarrow \text{H}_2\text{S}_2^+ + \text{H} \) reaction, which is well characterized (Anicich 2003). We note that \( \text{S}^+ \) and \( \text{SH}^+ \) are only abundant in the UV-irradiated gas (Gerin et al. 2016). Therefore, in spite of the large uncertainties in the reaction.
rates, we can conclude that these formation routes are only efficient in the UV-illuminated cloud surfaces.

5. Experimental Study of the Photodesorption of \( \text{S}_2\text{H} \) and \( \text{H}_2\text{S} \)

Jiménez-Escobar & Muñoz Caro (2011) showed that sulfur–sulfur bonds, in particular, \( \text{H}_2\text{S}_2 \) and \( \text{S}_2\text{H} \), are formed in irradiated ices. Here we focus on the determination of the \( \text{S}_2\text{H} \) and \( \text{H}_2\text{S} \) photodesorption yields, which are key to determine the origin (surface versus gas-phase chemistry) of the observed \( \text{S}_2\text{H} \). For this aim, we performed experimental simulations under astrophysically relevant conditions using the ISAC setup (Muñoz Caro et al. 2010), an ultra-high vacuum chamber with a work pressure on the order of \( 4 \times 10^{-11} \) mbar, corresponding to the pressure found in the interior of the pre-stellar cores. Sulfur is expected to be locked on the icy mantles in these regions, \( \text{H}_2\text{S} \) being the most abundant S-bearing molecule in cometary ices. Pure amorphous \( \text{H}_2\text{S} \) ice samples with thicknesses of about \( 40 \times 10^{15} \) molecules cm\(^{-2} \) were deposited from the gas phase (\( \text{H}_2\text{S} \) gas, Praxair, 99.8%) onto a KBr substrate at 8 K, and subsequently irradiated using an F-type microwave-discharged hydrogen flow lamp with a vacuum-ultraviolet flux of \( 2 \times 10^{14} \) photons cm\(^2\) s\(^{-1} \) at the sample position (Muñoz Caro et al. 2010). The emission spectrum of the lamp (reported in Chen et al. 2014, and Cruz-Díaz et al. 2014) resembles that of the secondary UV field in dense cloud interiors, calculated by Gredel et al. (1989). A Pfeiffer Prisma quadrupole mass spectrometer (QMS) was used during irradiation of the ice samples to monitor the mass fragments \( m/z = 34 \) (corresponding to photodesorbing \( \text{H}_2\text{S}_2 \) molecules) and \( m/z = 64 \) (corresponding to any desorbing photoproduc with a sulfur–sulfur bond, observed to form in Jiménez-Escobar et al. 2012). In our experiment, we did not monitor \( \text{S}_2\text{H} \) directly. However, if \( \text{H}_2\text{S}_2 \) or \( \text{S}_2\text{H} \) were desorbed, we would expect to detect all the fragments derived from these species, in particular \( \text{S}_2^+ \). While photodesorption of \( \text{H}_2\text{S} \) was detected, no gaseous \( \text{S}_2^+ \) was observed (see Figure 2). The measured ion current was converted into a photodesorption yield following calibration of the QMS (see Martín-Doménech et al. 2015). Photodesorption of \( \text{H}_2\text{S} \) took place with a decreasing yield, reaching a steady-state value of \( 1.2 \times 10^{-3} \) molecules per incident photon after \( 30 \) minutes of irradiation, which corresponds to the fluence experienced by ice mantles during the typical cloud lifetime (Shen et al. 2004). A factor of 2 is assumed as the error in the photodesorption yield values due to the uncertainties in the calibration process; see Martín-Doménech et al. (2016b). Following the non-detection of any sulfur–sulfur photoproduc, an upper limit of \( 1 \times 10^{-5} \) molecules per incident photon (the sensitivity limit of our QMS) was assumed for the photodesorption of \( \text{S}_2\text{H} \). Direct \( \text{S}_2\text{H} \) photodesorption or \( \text{H}_2\text{S}_2 \) photodissociation desorption are therefore not expected to be the origin of the gaseous \( \text{S}_2\text{H} \).

6. Discussion and Conclusions

At a distance of 400 pc, the Horsehead is a PDR viewed nearly edge-on and illuminated by the O9.5V star \( \sigma \) Ori at a projected distance of \( \sim 3.5 \) pc. The intensity of the incident FUV radiation field is \( \chi = 60 \) relative to the interstellar radiation field in Draine units. This PDR presents a differentiated chemistry from others associated with nearby H II regions such as the Orion Bar. One main difference is that the dust temperature is around \( 30 \) K in the PDR (Goicoechea et al. 2009), i.e., below or close to the sublimation temperature of many species, allowing a rich surface chemistry on the irradiated surfaces. Our unbiased line survey has provided valuable hints on the chemistry of this region. The detection of the molecular ions \( \text{CF}^+ \) and \( \text{HOC}^+ \) toward the HCO peak are well understood in terms of gas-phase photochemistry (Guzmán et al. 2012). We learned that there is an efficient top-down chemistry in the PDR, in which large polyatomic molecules or small grains are photodestroyed into smaller hydrocarbon molecules/precursors, such as \( \text{C}_2\text{H}, \text{C}_3\text{H}_2, \text{C}_3\text{H}, \) and \( \text{C}_3\text{H}^+ \) (Pety et al. 2012; Guzmán et al. 2015). The detection of several complex organic molecules (COMs) toward the warm (\( T_{\text{kin}} \sim 60 \) K) PDR and its associated

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**Table 2**

| Molecule   | HPBW (°) | \( T_{\text{rot}} \) (K) | \( N(X)/N_H \) | \( T_{\text{rot}} \) (K) | \( N(X)/N_H \) |
|------------|---------|---------------------------|----------------|---------------------------|----------------|
| \( \text{H}_2 \) | 12      | …                         | 2.9 \times 10^{-2} | 0.5                   | …              | 1.9 \times 10^{-2} | 0.5 |
| \( \text{S}_2\text{H} \) | 22–26  | 8.73^{+3.36}_{-1.36}    | 3.0^{+0.5}_{-0.6} \times 10^{12} | 5.2^{+1.5}_{-1.0} \times 10^{-11} | 12.69^{+3.18}_{-1.34} | 3.3^{+0.7}_{-0.6} \times 10^{12} | 8.7^{+1.3}_{-0.7} \times 10^{-11} |
| \( \text{H}_2\text{S}^+ \) | 14      | 9^{+1}_{-1}              | 1.9^{+0.3}_{-0.3} \times 10^{15} | 3.3^{+0.7}_{-0.6} \times 10^{-10} | 12^{+2}_{-2} | 1.2^{+0.3}_{-0.3} \times 10^{13} | 3.1^{+0.3}_{-0.3} \times 10^{-10} |

**Note.**

* We assume the rotation temperatures derived from \( \text{S}_2\text{H} \).
cold ($T_{\text{kin}} \sim 20$ K) core was unexpected. In fact, the chemical complexity reached in the Horsehead is extraordinarily high with COMs of up to seven atoms: HCOOH, H$_2$CCO, CH$_3$CHO, and CH$_3$CCH (Guzmán et al. 2014). Current pure gas-phase models cannot reproduce the inferred H$_2$CO, CH$_3$OH, and COMs abundances in the Horsehead PDR (Guzmán et al. 2011, 2013), which supports the grain-surface origin of these molecules. Le Gal et al. (2017) was able to reproduce the observed COMs abundances using a chemical model with grain-surface chemistry and found that chemical desorption, instead of photodesorption, is the main process to release COMs to the gas phase. CH$_3$CN and CH$_3$NC, key species for the formation of prebiotic molecules, seem to have a very specific formation pathway in the PDR (Gratier et al. 2013). The Horsehead is therefore an excellent site to study the influence of UV radiation on the grain-surface chemistry and its subsequent impact on the gas phase.

We present the first detection of S$_2$H in the Horsehead. The observed S$_2$H abundance is $5 \times 10^{-11}$, only a factor of 4–6 lower than that of H$_2$S. Our laboratory experiments show that the H$_2$S and S$_2$H photodesorption yields are $1.2 \times 10^{-2}$ and $<1 \times 10^{-5}$ molecules per incident photon, respectively. Although S$_2$H can be formed on warm ($T_d > 15$ K) grains, our upper limit to the S$_2$H photodesorption yield suggests that this mechanism is not efficient to release the S$_2$H molecules from the grain mantles. Other desorption mechanisms such as chemical desorption, cosmic-ray desorption, and grain shattering could increase the S$_2$H abundance in the gas phase. S$_2$H can also be formed in the gas phase by reactions involving H$_2$S and the ions S$^-$ and SH$.^+$ These ions are expected to be abundant in the external layers of the PDR (Goicoechea et al. 2006). The photodesorption of H$_2$S could hence boost the S$_2$H production in the gas phase. We conclude that the abundance of S$_2$H in the Horsehead is more likely the consequence of the favorable physical conditions prevailing in this nebula where grain mantles irradiated by UV photons coexist with the ions S$^+$ and SH$^+$ that are only abundant in PDRs.

One interesting issue is to compare the sulfur and oxygen chemistry. We have not detected H$_2$S$_2$, HSO, H$_2$O$_2$, and HO$_2$ in the Horsehead with the upper limits shown in Table 3. We find interesting that the column densities of HSO and HO$_2$ are lower than that of S$_2$H, although the oxygen elemental abundance is 30 times greater than that of sulfur. In the gas phase, S$_2$H is mainly formed through S$^+$ + H$_2$S $\rightarrow$ HSO + H and SH$^+$ + H$_2$S $\rightarrow$ HS$^+$ + H, followed by dissociative recombination of HS$^+$. Oxygen and sulfur have indeed similar reactivity, but due to their different ionization potentials, O$^+$ is less abundant than S$^+$ in the PDR. Hence, reactions involving O$^+$ play a smaller role. In addition, reactions of OH$^-$ and H$_2$O$^+$ with H$_2$O do not lead to the formation of H$_2$O$_2$ (Anicich 2003), thus to the formation of HO$_2$. We have also compared the SH$^+$ + H$_2$O and SH$^+$ + H$_2$S gas-phase reactions, which may be intermediate paths at work for producing SOH and S$_2$H, respectively. The channel toward the HSO$^+$ + H$_2$ reaction is endothermic in opposition to the channels toward S$_2$H$^+$ + H and S$_2$H$_2^+$ + H. Therefore, in the gas phase, the formation of S$_2$H is favored relative to HSO. HSO and related species have not been observed in space thus far (Cazzoli et al. 2016; Fortenberry & Francisco 2017). Laboratory experiments demonstrate that grain-surface chemistry involving H$_2$O and H$_2$S also present different pathways. Photodesorption experiments reported by Cruz-Diaz et al. (2017) show that H$_2$O$_2$ is not formed in UV-irradiated water ice. In contrast, Jiménez-Escobar & Muñoz Caro (2011) showed that S$_2$S$_2$ is formed when H$_2$S and H$_2$S–H$_2$O ices are irradiating, providing a path to form species with two sulfur atoms. In summary, sulfur and oxygen are not analogs in the gas-phase and surface chemistry, and the comparison of their related species requires the full chemical modeling of the region.

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