Ultraviolet photolysis of H$_2$S and its implications for SH radical production in the interstellar medium

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Hydrogen sulfide radicals in the ground state, SH(X), and hydrogen disulfide molecules, H$_2$S, are both detected in the interstellar medium, but the returned SH(X)/H$_2$S abundance ratios imply a depletion of the former relative to that predicted by current models (which assume that photon absorption by H$_2$S at energies below the ionization limit results in H + SH photoproducts). Here we report that translational spectroscopy measurements of the H atoms and S(1D) atoms formed by photolysis of jet-cooled H$_2$S molecules at many wavelengths in the range $122 \leq \lambda \leq 155$ nm offer a rationale for this apparent depletion; the quantum yield for forming SH(X) products, $\Gamma$, decreases from unity (at the longest excitation wavelengths) to zero at short wavelengths. Convoluting the wavelength dependences of $\Gamma$, the H$_2$S parent absorption and the interstellar radiation field implies that only ~26% of photoexcitation events result in SH(X) products. The findings suggest a need to revise the relevant astrochemical models.
Sulfur is one of the more abundant elements in the Universe (S/H ≈ 1.3 × 10^{-5} in the solar photosphere), but the abundances of known sulfur-containing molecules in the interstellar medium (ISM) sum to well below this value. Estimates based on the limited number of S-containing compounds detected in diffuse clouds imply a sulfur abundance in such low-density regions not far from the cosmic value. However, the abundance of S-containing species in the external layers of the photodissociation region (PDR) in the Horsehead nebula, for example, is deduced to be ~4-fold depleted (cf. the cosmic value) and one or more orders of magnitude depletions have been reported in cold molecular clouds. Such extreme depletions have been reported not only in cold pre-stellar cores (where most of the sulfur may be locked in icy mantles), but also in hot cores/corinos where one might expect much of the sulfur to have returned to the gas phase in hot cores and strong shocks — though we note that such conclusions can be very sensitive to assumptions regarding the chemical composition prior to collapse. Given the high-hydrogen abundances and the mobility of hydrogen in the ice matrix, sulfur atoms impinging on interstellar ice mantles are expected to preferentially form H2S, the chemical- and photo-desorption of which constitutes a source of electronic term values of cold pre-stellar cores (where most of the sulfur may be locked in icy mantles) and strong shocks — though we note that such conclusions can be very sensitive to assumptions regarding the chemical composition prior to collapse. Given the high-hydrogen abundances and the mobility of hydrogen in the ice matrix, sulfur atoms impinging on interstellar ice mantles are expected to preferentially form H2S, the chemical- and photo-desorption of which constitutes a source of electronic term values.

In addition, there was an earlier report of isotopic fractionation in solid sulfur films deposited following broadening (~2 nm), non-collision-free photodissociation of slowly flowing samples of H2S gas at several VUV wavelengths.

Herein, we present a photochemical rationale for the deduced paucity of SH radicals in PDRs of the ISM based on the predisposition of much of the primary SH photoproducts. The study employed the intense, pulsed vacuum ultraviolet (VUV)-free electron laser (FEL) at the Dalian coherent light source (DCLS) to measure product state-resolved translational energy spectra of both the H and S(D) atom photoproducts formed following tunable VUV photolysis of H2S using, respectively, the H-atom Rydberg tagging and velocity map ion imaging techniques. The experimental results imply that only ~26% of photoexcitation events result in SH(X) products.

Results and discussion

Product translational energy distributions. H atom time-of-flight (TOF) spectra were recorded following photolysis of a jet-cooled H2S sample at many wavelengths resonant with its discrete VUV absorption peaks. These spectra were converted to the corresponding H atom translational energy distributions, and momentum conservation arguments were then used to derive the total translational energy distributions, \( P(E_T) \), where

\[
E_T = \frac{1}{2} m_H \left( \frac{d^2}{7} \right) \left( 1 + m_H/m_S \right),
\]

\( m \) is the photofragment mass, \( d \) is the distance separating the interaction region and the detector, and \( \hbar \) is the H atom TOF measured over this distance. Figure 1 shows \( P(E_T) \) spectra obtained at \( \lambda = (a) \) 154.53 nm (64712 cm⁻¹), (b) 139.11 nm (71886 cm⁻¹), and (c) 122.95 nm (81334 cm⁻¹). The polarization vector of the photolysis laser radiation \( (\epsilon_{\text{photon}}) \) used to record these spectra was aligned at the magic angle \( (\theta = 54.7°) \) to the detection axis, thereby ensuring that the spectra are insensitive to the product channel dependent recoil anisotropies revealed by spectra taken with \( \epsilon_{\text{photon}} \) aligned, respectively, parallel \((\theta = 0°)\) and perpendicular \((\theta = 90°)\) to the detection axis. The inset in Fig. 1b illustrates such recoil anisotropy for the products of photolysis at \( \lambda = 139.11 \) nm. H atom TOF spectra recorded at all three wavelengths with \( \epsilon_{\text{photon}} \) aligned at \( \theta = 0° \) and \( 90° \) are shown in Supplementary Fig. 1, but detailed descriptions of the rovibronic structure of the SH radical and of the photofragmentation dynamics responsible for the populations and recoil anisotropies of the various SH products formed when exciting H2S at many different wavelengths in the range 122 ≤ \( \lambda \) ≤ 155 nm are reserved for a future publication. Here we choose to highlight just the following features:

i. The SH fragments formed at \( \lambda = 154.53 \) nm are in their ground \((X)\) state, reinforcing the findings of prior photofragmentation studies at \( \lambda = 157.6 \) nm and at all longer wavelengths. The combs festooned above the spectrum show that the SH\((X)\) population is distributed over a wide range of quantum states, spanning rotational \((N)\) levels of most if not all vibrational \((v)\) levels. The SH\((X)\) potential energy curve correlates with H + S(3P) fragments at infinite separation and the small feature at low \( E_T \) in Fig. 1a is consistent with three-body dissociation to H + S (3P) products, the threshold energy for which \((\Delta E(3))\) lies ~1600 cm⁻¹ below that for two-body dissociation to H + SH(A) products.

ii. \( \lambda = 139.11 \) nm photolysis yields both SH\((X)\) and SH\((A)\) fragments. The latter are revealed by the sharp step at \( E_T = E_{\text{photon}} - \Delta E(2) \), where \( E_{\text{photon}} \) is the photolysis photon energy and \( \Delta E(2) \) is the threshold energy for forming H + SH(A)}
products. The SH(A) fragments formed at this wavelength are mainly in their \( v' = 0 \) level but carry high levels of rotational excitation. \( \lambda = 149.15 \text{ nm} \) was the longest photolysis wavelength at which structure unambiguously attributable to \( \text{H} + \text{SH}(A) \) products was observed.

iii. SH(A) fragments dominate when exciting at \( \lambda = 122.95 \text{ nm} \), as at 121.6 nm\(^\text{25} \). The combs in Fig. 1c show that the SH(A) fragments are formed mostly in low \( v \) levels but have rotational state distributions that extend to the highest \( N' \) levels supported by the SH(A) potential energy function\(^\text{25} \). Note that these highest \( N' \) levels have rotational energies well in excess of the bond dissociation energy of the SH(A) state—indicated by the \( S(1D) + 2 \text{H} \) arrow in Fig. 1c—and that the signal at lowest \( E_T \) in Fig. 1c must include contributions from direct three-body-dissociation to such products. Population of similar “super-rotor” levels (i.e., rotational levels that are only quasi-bound by virtue of the centrifugal barrier associated with the high-rotational angular momentum) has also been reported recently in the case of \( \text{OH}(X) \) products arising in the VUV photolysis of \( \text{H}_2\text{O}\)^\text{32} \).

iv. SH(A) state radicals predissociate on a nanosecond (or shorter) timescale to yield \( \text{H} + S(3P) \) atom products\(^\text{35} \). Thus, every primary SH(A) photofragment will dissociate to yield a second H atom during the time that the Rydberg tagging laser radiation is present. Such secondary H atoms must contribute to the measured H atom TOF spectra and the \( P(E_T) \) spectra derived therefrom. The predissociation of SH(A) radicals favors population of the ground \( (J=2) \) spin-orbit state of the \( S(3P) \) product\(^\text{35} \), and a comb indicating the expected \( E_T \) values of \( \text{H} + S(3P) \) products from predissociation of different SH(A, \( v' = 0, N' \) ) levels formed in the \( \lambda = 139.11 \text{ nm} \) photolysis of \( \text{H}_2\text{S} \) is also included in the inset to Fig. 1b.

The term \( (E_{\text{phot}} - \Delta E(3)) \), henceforth written as \( E_T(3) \), will prove to be a useful point at which to divide \( P(E_T) \) spectra such as those shown in Fig. 1. All signal measured at \( E_T > E_T(3) \) is associated with branching into \( \text{H} + \text{SH}(X) \) products, while signal at \( E_T < E_T(3) \) must be associated with three-body dissociation, yielding two H atoms—either directly, or indirectly when the second H atom comes from the predissociation of a primary SH(A) photoproduct. Thus, we can define the following fraction, \( \Gamma \), for forming SH(X) products following VUV photoexcitation of \( \text{H}_2\text{S} \):

\[
\Gamma = \frac{\sum P(E_T > E_T(3))}{\sum P(E_T > E_T(3)) + 0.5 \sum P(E_T < E_T(3))}
\]
where the 0.5 in the second term in the denominator recognizes that, for this fraction of the product yield, the absorption of one photon yields two detectable H atom products. This partitioning would not be perfect if, for example, dissociation at some wavelengths resulted in a (small) yield of SH(X) super-rotor states, but it allows a good estimation of the wavelength dependence of Γ. The implications of the derived Γ(λ) function for interstellar SH number densities are considered later.

**Imaging the S(1D) + H₂ products.** Figure 2a shows a time-sliced velocity map image of the S(1D) atoms formed following photolysis of a jet-cooled H₂S sample at λ = 139.11 nm, with £phot aligned in the plane of the image (as indicated by the red arrow) and subsequent resonant ionization by absorption of a single λ = 130.091 nm photon. The latter photons were generated by four wave difference frequency mixing, by overlapping the focussed outputs of two table-top dye lasers operating at λ = 212.556 nm and λ = 580.654 nm in a Kr/Ar gas mixture. Image analysis yields the velocity distribution, and thence the corresponding P(Efi) distribution shown in Fig. 2b assuming momentum conservation and that the partner fragment is H₂. The image appears isotropic. The P(Efi) spectrum is structured and peaks at Efi ~ 0, demonstrating preferential population of high v’ and j’ levels of the H₂ fragments (henceforth represented as H₂j’)—as shown by the combs above the spectrum in Fig. 2b. This finding conforms and extends conclusions reached in an early resonance enhanced multiphoton ionization study of the H₂ molecules formed via two-photon dissociation of H₂S at similar overall excitation energies.

The H₂(X) potential correlates with two ground state H atoms at infinite separation and, recalling Eq. (4), the energetic threshold for the triple fragmentation of H₂S to 2H + S(1D) products is ~1960 cm⁻¹ below the energy provided by a 139.11 nm photon. Any such three-body dissociation should thus be revealed by signal appearing with Efi < 1960 cm⁻¹ in Fig. 2. This spectrum shows no obvious step or discontinuity at low Efi values, but such signal is apparent (as a bright central spot) in S(1D) atoms formed following photolysis of a jet-cooled H₂S sample at λ = 139.11 nm ≤ 0.12 and that S–H bond fission is the dominant primary event at this wavelength.

The fragmentation dynamics. As noted previously, detailed discussion of the fragmentation dynamics revealed by the present measurements will be reserved for a future publication, but many aspects of the observed product energy disposal are seen to be qualitatively similar to those found in previous studies of the lighter analog, H₂O. As in H₂O, the two key valence absorption continua that support HS–H bond fission arise from excitation of an electron from the highest occupied molecular orbitals (the HOMO, 3px and HOMO–1, 3pz (with b₁ and a₁ symmetry, respectively, in C₂v)) to the 4s (a₁) Rydberg orbital. The 4s orbital acquires progressively greater anti-bonding valence σ* character on stretching one S–H bond. The 1B₁ and 1A₁ states formed by these electron promotions, which we henceforth label A and B to emphasize the parallels with H₂O, are a Renner–Teller pair and degenerate at linear geometries. Both correlate with ground state H + SH(X) products at linear geometry (and the ground 1B₁, 1A₁ state of H₂S correlates with excited H + SH(A) products). However, the A and B states split apart on bending. The A state potential energy surface (PES) is relatively flat with respect to changing the interbond angle, χ(HSH), but the B state potential rises in energy and its crossings with the X state PES at extended HS–H (and H–HS) bond lengths develop into conical intersections (CIs) upon bending away from linearity. At all non-linear geometries, therefore, the B state PES correlates with electronically excited SH(A) products.

The ground state and the Rydberg (R) states of current interest all have bent equilibrium geometries (χ(HSH) ~ 92°). The R states are diabatically bound with respect to HS–H bond extension but,
as with H₂O molecules excited to the C ¹B₁ state, H₂S (R) molecules prepared at longer excitation wavelengths would be expected to dissociate via the former, lower energy pathway to yield H + SH(X) products in a range of υ levels but with relatively modest rotational excitation—in accord with experimental observation at λ = 154.53 nm, for example.

These various fragmentation pathways are all illustrated schematically in Fig. 3 for the case of H₂S excitation with a VUV photon of intermediate energy, e.g., 139.11 nm. The topography of the B state PES encourages high-rotational excitation in the SH(A) products and vibrational excitation in the H₂⁺ products from the respective two-body fragmentations—outcomes that are accentuated further by tuning to shorter wavelengths. The present discussion suggests that three-body dissociation to 2H + S(1D) products at shorter photolysis wavelengths can arise via two distinct mechanisms involving, respectively, initial distortions towards H----SH(A) products in the vicinity of CI1 and towards S----H₂⁺ products around CI2.

Implications for SH densities in the interstellar medium. The present imaging studies show that the S(1D) + H₂ product channel is active at λ = 139.11 nm (and at neighboring wavelengths), but with a rather small quantum yield, thus confirming that S-H bond fission is the dominant primary event following photoexcitation of H₂S at VUV wavelengths. However, S-H bond fission can result in several final outcomes (channels (1)-(4)), only one of which yields stable SH(X) products. The H-atom Rydberg tagging studies show Γ decreasing from 1 (at λ ≥ 157.6 nm) to 0 (by λ ≤ 121.6 nm). Figure 4 collects together the wavelength dependences of: Γ determined in the present study; the general interstellar radiation field (ISRF, from Draine) and extended according to van Dishoeck and Black; and the total photoabsorption and photoionization cross-sections of the parent H₂S molecule (σₒtot and σₒot respectively) down to the wavelength corresponding to the ionization threshold of atomic H (λ = 91.2 nm). Note, the very short lived nature of the excited states populated at all wavelengths implies that the photodissociation and photoabsorption cross-sections are identical at all λ > 118.4 nm.

The peak of the ISRF matches with the region of strong parent absorption, within which Γ is changing rapidly. Reference to Fig. 4 shows that absorption at wavelengths below the ionization limit (λ ≤ 118.4 nm) will increasingly result in ionization, but any dissociative ionization at λ > 91.2 nm will yield S+ or SH⁺ products (i.e., no neutral SH(X) products). It is thus reasonable to assume Γ = 0 at all wavelengths in Fig. 4 shorter than those studied in the present work, and to estimate the fraction ϕ of all photoexcitation events that result in SH(X) fragments by convoluting Γ with the standard model of the ISRF and with σₒtot. The uncertainty in Γ can be quantified (12.5%, defined as the normalized (by range) root-mean-square error from the fitted sigmoidal function), but to estimate an uncertainty on ϕ also requires knowledge of the λ-dependent uncertainties associated with the ISRF and with σₒtot. These are not available, but are likely dominated by the uncertainty in the form of the ISRF, which is quoted as being “within about 50%”. From all the foregoing, ϕ is definitely <1, with a best estimate of ϕ ~26% based on the wavelength dependent functions displayed in Fig. 4. The largest source of uncertainty in ϕ is likely to be that associated with the ISRF, which is necessarily high for it to represent the galactic average. However, the remaining quantities are invariant for H₂S molecules anywhere in the universe and a more precise value of ϕ

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**Fig. 3** Potential energy surface contour plots of H₂S. Potential energy surface of the B state of H₂S plotted as a function of Rₛ–H (the distance of the departing H atom from the S atom, with the other S-H bond held fixed at the ground state equilibrium bond length (2.5 bohr)) and the interbond angle ϕ. The contour labels are given in units of 10⁻³ cm⁻¹, with the energy zero calculated at Rₛ–H = 100 bohr (i.e., the H + SH(X) dissociation limit). The two regions of conical intersection with the X state PES at linear H–S–H and S–H–H geometries (CI1 and CI2, respectively) are highlighted in red. The green curves show illustrative type I, II and III trajectories originating from the region sampled by vertical Franck-Condor excitation at the ground state equilibrium geometry. Source data are provided as a Source Data file.
Methods

Vacuum ultraviolet free electron laser (VUV-FEL) radiation. The experiment employs a recently constructed apparatus for molecular photochemistry centered on a VUV-FEL facility49 operating in the high gain harmonic generation (HGHG) mode47, wherein a seed laser is injected to interact with the electron beam in the modulator. The seed laser pulse (in the range 240 < λ\text{seed} < 360 nm) is generated from a picosecond (ps) Ti:sapphire laser. The electron beam is generated from a photocathode radio frequency gun and accelerated to a beam energy of ~300 MeV by 7 S-band accelerator structures, with a bunch charge of 500 pC. The micro-bunched beam is sent through the radiator which is tuned to the nth harmonic of the seed wavelength and coherent FEL radiation with wavelength λ\text{seed}/n is emitted. Optimizing the linear accelerator results in a high-quality beam with emittance ~1.5 mm·mrad, a projected energy spread of ~1‰, and pulse duration of ~1.5 ps.

The VUV-FEL currently operates at 10 Hz, the maximum pulse energy is ~500 µJ pulse and with a specified continuous tunability range of 50 < λ < 150 nm and a typical spectral bandwidth of ~50 cm⁻¹. However, as the present study shows, the stated long wavelength limit can be slightly exceeded.

The H-atom Rydberg tagging TOF technique, pioneered by Welge and coworkers96, employs a sequential two-step excitation of the H atom on, first, the n = 2+\n transition by absorption of a 121.6 nm photon, then by UV laser excitation (365 nm) from the n = 2 level to a high-\n Rydberg state. The neutral Rydberg atoms fly a distance d = 280 mm to a rotatable microchannel plate (MCP) detector where they are field ionized, giving a TOF temporal resolution of <0.5%. The sample beam was generated by expanding a mixture of 1% H₂S and Ar at a stagnation pressure of 600 Torr through a 0.5 mm-diameter pulsed nozzle. The molecular beam crosses the VUV-FEL beam at right angles. The polarization of the VUV-FEL pulse is fixed in the horizontal plane, so “parallel” and “perpendicular” TOF spectra are obtained by rotating the MCP detector about the VUV-FEL propagation axis. The 121.57 nm tagging laser beam generates a background H atom spectrum also, which is measured by recording spectra with the VUV-FEL beam on and off and subtracted accordingly.

The apparatus and most of the procedures for the velocity map imaging (VMI) experiments have been described in the Supplementary Fig. 3 and Supplementary note 251,52. The pulsed supersonic beam was again generated by expanding a mixture of 1% H₂S and Ar into the source chamber where it was skimmed before entering (through a 2 mm hole in the first electrode), and propagating along the center axis of, the ion optics assembly mounted in the same differentially pumped reaction chamber. The molecular beam was intersected at right angles by the photolysis and probe laser beams between the second and the third plates of the ion optics assembly. The photolysis photons were provided by the FEL with, again, e\text{short} fixed in the horizontal plane and thus parallel to the front face of the detector. The S⁺(1D\text{g}) photoproducts are probed by one photon excitation at λ = 130.91 nm, which populates the autoionizing 3p(5/D\text{g}) + 1D\text{g} level. These latter photons were generated by four wave difference mixing the frequency doubled output of a dye laser (at λ = 212.556 nm) with the fundamental output of a second dye laser (at λ = 580.654 nm) in a Kr/Ar gas mixture. The S⁺(1D\text{g}) ions are accelerated through the remaining ion optics and a 740 mm long field-free region before impacting on a 70 mm-diameter chevron double MCP detector coupled with a P43 phosphor screen. Transient images on the phosphor screen were recorded by a charge-coupled device (CCD) camera, using a 30 ns gate pulse voltage in order to acquire time-sliced images. Further details of the FEL–VMI experiments are provided in the Supplementary Information.

Data availability

The data supporting this study are available from the authors on reasonable request. The source data underlying Figs. 1–4 are also provided as a Source Data file.

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