

RESEARCH ARTICLE | JANUARY 12 2024

Energetic processing of thioacetamide in cryogenic matrices



Sándor Góbi ; Barbara Keresztes ; Anita Schneiker ; Gopi Ragupathy ; György Tarczay



J. Chem. Phys. 160, 024310 (2024)

<https://doi.org/10.1063/5.0177587>



CrossMark



Chemical Physics Reviews

Special Topic: Molecular Approaches
for Spin-based Technologies

Submit Today!

AIP
Publishing

Energetic processing of thioacetamide in cryogenic matrices

Cite as: J. Chem. Phys. 160, 024310 (2024); doi: 10.1063/5.0177587

Submitted: 22 September 2023 • Accepted: 11 December 2023 •

Published Online: 12 January 2024



Sándor Góbi,^{1,2,a)} Barbara Keresztes,^{2,3} Anita Schneiker,^{2,3} Gopi Ragupathy,^{1,b)}
and György Tarczay^{1,2,4}

AFFILIATIONS

¹ MTA-ELTE Lendület Laboratory Astrochemistry Research Group, Institute of Chemistry, ELTE Eötvös Loránd University, P.O. Box 32, H-1518 Budapest, Hungary

² Laboratory of Molecular Spectroscopy, Institute of Chemistry, ELTE Eötvös Loránd University, P.O. Box 32, H-1518 Budapest, Hungary

³ Hevesy György PhD School of Chemistry, Institute of Chemistry, ELTE Eötvös Loránd University, P.O. Box 32, H-1518 Budapest, Hungary

⁴ Centre for Astrophysics and Space Science, ELTE Eötvös Loránd University, P.O. Box 32, H-1518 Budapest, Hungary

Note: This paper is part of the 2023 JCP Emerging Investigators Special Collection.

^{a)} **Author to whom correspondence should be addressed:** sandor.gobi@ttk.elte.hu

^{b)} **Present address:** School of Advanced Sciences (SAS), Vellore Institute of Technology, Vellore Campus, Vellore 632014, Tamil Nadu, India.

ABSTRACT

There is an ongoing debate on the apparent depletion of sulfur in the interstellar medium (ISM) compared to its universal abundance; therefore, the investigation of sulfurous compounds at low temperatures is of utmost importance. This work aims to study thioacetamide, $\text{H}_3\text{C}-\text{C}(=\text{S})-\text{NH}_2$, in low-temperature inert Ar and *para*- H_2 matrices by IR spectroscopy. The samples have been exposed to various sources of irradiation, such as Lyman- α or laser UV photons as well as energetic electrons. Using different host materials enabled assessing the matrix's impact on precursor decomposition. The response of the molecule to different types of irradiation has also been evaluated. The existence of three main decomposition channels were deduced: formation of (i) CH_3 , CH_4 , and HNCS ; (ii) H_2S and $\text{H}_2\text{C}=\text{C}=\text{NH}$; and (iii) NH_3 and $\text{H}_2\text{C}=\text{C}=\text{S}$. The $\text{H}_3\text{C}-\text{CN}$ and $\text{H}_3\text{C}-\text{NC}$ isomers of $\text{H}_2\text{C}=\text{C}=\text{NH}$ could also be identified. Secondary products such as HNC and HCN were also detected in the quantum solid *para*- H_2 in contrast to the more rigid Ar matrix. The listed decomposition products have been observed in the ISM, with the exception of $\text{H}_2\text{C}=\text{C}=\text{NH}$ and $\text{H}_3\text{C}-\text{NC}$. The results point to the potential sensitivity of the precursor molecule to energetic radiation in space environments. Finally, the findings of this work will serve as a foundation for future irradiation experiments using the astrochemically more relevant pure thioacetamide ice.

Published under an exclusive license by AIP Publishing. <https://doi.org/10.1063/5.0177587>

I. INTRODUCTION

Sulfur is the tenth most abundant element by mass in the universe, with an estimated mass fraction of 440 ppm. Although space is a harsh environment with various ionizing radiation sources, numerous sulfurous compounds have been detected over the past decades. Yet, there is a huge discrepancy of three orders of magnitude between the cosmic abundance of sulfur and that observed in the interstellar medium (ISM) or protoplanetary disks,^{1–3} which may be eventually overcome by improving the current chemical models and conducting

laboratory studies focusing on sulfurous compounds.^{4–6} Despite this apparent scarcity of sulfur in such environments, there is an ever-growing number of detected sulfur-containing species in them.⁷

A candidate molecule, which can be important from this perspective, is thioacetamide ($\text{C}_2\text{H}_5\text{NS}$, see exact structures of its tautomers in Fig. 1).^{8,9} This sulfur-bearing compound has undergone extensive investigation. Low-temperature IR spectra of thin films have been studied in various instances.^{10–12} Additionally, matrix-isolation studies were carried out, with a focus on thione–thiol [$\text{H}_3\text{C}-\text{C}(=\text{S})-\text{NH}_2$ vs $\text{H}_3\text{C}-\text{C}(-\text{SH})=\text{NH}$] tautomerization induced

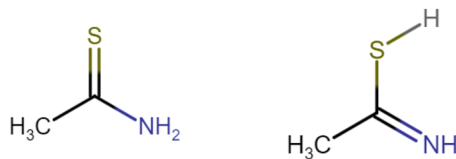


FIG. 1. Schematic representation of the thione (left) and the thiol (right) tautomers of thioacetamide.

by UV irradiation of samples in inert matrices.¹³ The excited state proton transfer dynamics of thioacetamide (thione–thiol phototautomerization) in solution phase, accompanied by quantum mechanical computations, has also been studied previously. The authors found an absorption maximum at ~ 266 nm (depending on the solvent) and proposed a mechanism via the $S_{2,FC} \rightarrow S'_{1,min}$ excited state proton transfer (ESPT) reaction channel.¹⁴ Other research studies have explored the spontaneous conversion of thiols via H atom tunneling¹⁵ and conformational switching. This switching involved selective changes in the geometry of remote functional groups achieved by exciting the NH_2 stretching vibrational overtone of the thiol conformers with near-IR (NIR) laser irradiation.¹⁶ During our above-mentioned previous works involving UV irradiation, the formation of a small fraction of photolysis products was always observed but remained unidentified as it was beyond the scope of those works.

The proper modeling of decomposition processes due to exposure to high-energy radiation such as galactic cosmic rays (GCRs), solar wind particles, or UV photons is extremely relevant, having its own vast literature in the field of laboratory astrophysics. Since the IR bands in condensed phase are usually poorly resolved and overlap with each other,¹⁷ the interpretation can be facilitated if the preliminary photolytic experiments are conducted as matrix-isolation studies, where the molecules are diluted and isolated from each other in a low-temperature inert matrix, resulting in the enhancement of the spectral resolution. Furthermore, due to the inert media, the primary decay products, which are usually reactive transient species such as radicals, can be trapped in the matrix, allowing for their detection by means of, for instance, IR spectroscopy, leading to a better understanding of molecular decomposition mechanisms. Historically, solid Ar was the most frequently used matrix besides other frozen noble and/or inert gases, such as Kr, Xe, N_2 , but more exotic molecules such as *para*- H_2 can also be used. Low-temperature *para*- H_2 is also called quantum solid owing to its unique physical and chemical properties and has been garnering more attention recently as a matrix host material. One of the main advantages of carrying out experiments in *para*- H_2 matrix is that the molecular interactions are even weaker than in traditional noble gas or inert gas matrices, resulting in even sharper spectral bands. Another is the diminished cage effect, which allows for the formation and detection of species that could not be observed otherwise.¹⁸

Still, apart from the most basic sulfur compounds, such as sulfur dioxide (SO_2),^{19–21} sulfur trioxide (SO_3),²² hydrogen sulfide (H_2S),²³ hydrogen disulfide (H_2S_2),²⁴ the HSO_2 isomers,²⁵ as well as carbonyl sulfide (OCS) and carbon disulfide (CS_2),²⁶ no extensive photolytic studies have been performed for more complex molecules of astrophysical interest isolated in inert matrices, except

for methanethiol (CH_3SH),²⁷ ethanethiol (C_2H_5SH),²⁸ and mercaptoacetoneitrile ($HS-CH_2-C\equiv N$).²⁹ Accordingly, this work aims to shed light on the photolytic behavior of thioacetamide in Ar and *para*- H_2 matrices upon its exposure to various types of energetic radiation. The use of different inert matrices ensures proper assessment of the effect of the matrix surrounding sample molecules. Lyman- α is an important radiation source that has been used for decades to mimic interstellar UV radiation fields in laboratory astrochemistry.³⁰ Nevertheless, multiple laser UV spectral wavelengths are also used, allowing for the evaluation of existing decomposition channels and the wavelength-dependence of their relative rates. The third radiation source, the electron gun, aims to mimic the secondary electrons forming when galactic cosmic rays interact with matter (see, e.g., Ref. 31).

II. MATERIALS AND METHODS

The matrix-isolation experiments were performed with the help of the VIZSLA setup consisting of an ultrahigh-vacuum (UHV) compatible stainless steel chamber with a base pressure of 1×10^{-9} mbar when cooled.³² For the experiments, Ar (Messer, 99.9999%) and *p*- H_2 were used. *p*- H_2 was prepared by flowing *n*- H_2 (Messer, 99.9999%) through porous Fe(III) oxide (Sigma-Aldrich, (St. Louis, MI, USA), hydrated, catalyst grade, 30–50 mesh) cooled down to 13.9 K wrapped around the upper cold head of the setup (CH202, Sumitomo Heavy Industries, Inc.). All gases were stored in a 0.5 l glass flask connected to a separate gas mixing line. The thioacetamide sample was inserted into a small glass vial directly attached to the vacuum chamber separated by a valve.

The matrix was prepared by co-depositing thioacetamide and the carrier gas on a gold-coated silver wafer serving as the substrate mounted on the cold finger of the lower cold head (RDK-415D, Sumitomo Heavy Industries, Inc.). For this, the temperature of thioacetamide was kept between 15 and 20 °C during deposition and was introduced through a Teflon tube 6 mm in diameter ending ≈ 3 cm before the substrate. The matrix gases were introduced to the vacuum chamber via a stainless steel capillary array through a leak valve; the distance between the substrate and the end of the capillaries was also roughly 3 cm. Inlet rates of the matrix gases were 0.3–0.5 mbar l min^{−1} when using Ar and 0.8–1.1 mbar l min^{−1} when using *p*- H_2 , respectively.

Both the Ar and *p*- H_2 matrices underwent separate experiments involving Lyman- α , selective UV laser irradiation, and energetic electron bombardment. A microwave discharge H atom lamp ($P = 100$ W, $p(H_2) \approx 0.4$ mbar) was used as Lyman- α source, whereas a Specs EQ 22 electron gun served as the high-energy electron source (electron kinetic energy was set to ≈ 5 keV, nominal emission current was kept at 100 nA). The Lyman- α irradiation was run for ≈ 2 h on the already deposited matrices, whereas the electron irradiation was done during deposition, which lasted roughly 1.5 (Ar matrix) and 3 h (*p*- H_2 matrix), respectively. The UV laser irradiation studies were carried out by an optical parametric oscillator (OPO, GWU/Spectra-Physics VersaScan MB 240, FWHM ≈ 5 cm^{−1}) equipped with a frequency-doubling unit (Spectra-Physics uvScan) pumped by a pulsed Nd:YAG laser (Spectra-Physics Quanta Ray Lab 150, $P \approx 2.0$ W, $\lambda = 355$ nm, $f = 10$ Hz, pulse duration = 2–3 ns). A lens is typically put between the aperture of the laser setup and the substrate, making the laser beam profile more spread out, thus

reducing the photon flux and the heat load on the sample. The irradiation wavelengths were 300, 270, 240, and 216 nm, respectively; the exposure times were typically 30 min. One exception was after the 216 nm irradiation in *para*-H₂ when the irradiation was repeated at the same wavelength for another 70 min with the above-mentioned lens removed, thus focusing all the laser beam on the sample. Blank experiments were also conducted when the sample was not exposed to any kind of radiation. All the deposition/irradiation cycles were performed at 15 K in the case of Ar and at 3.1 K for the *p*-H₂ experiments, respectively.

The mid-IR (MIR) spectra were taken by a Bruker Invenio FT-IR spectrometer working in reflection-absorption mode and equipped with a liquid N₂-cooled mid-band Mercury Cadmium Telluride (MCT) detector. Each spectrum was collected in the spectral region of 4000–600 cm⁻¹ at a resolution of 1 cm⁻¹ in the case of Lyman- α photolysis and 5 keV electron bombardment. In every phase of the experiment (deposition and irradiation), 32 scans were averaged in each minute. The background spectra were collected just before the deposition at the same temperature and resolution as during the experiment, averaging 256 scans. The spectral resolution was set to 0.5 cm⁻¹ for the laser irradiation experiments using the same amount of averaged scans as detailed previously.

Assignment of the vibrational spectra of irradiation products was mainly done based on the Ar-matrix and gas-phase data found in the literature supported by the band kinetics upon irradiation, i.e., with the assumption that IR absorption bands with identical temporal evolution belong to the same species. In order to estimate the mixing ratios, the computed anharmonic vibrational intensities were used. For this, quantum-chemical DFT computations were carried out with the Gaussian 09 software (Rev. D01).³³ The geometry of the structure of thioacetamide and the possible photolysis products at the minima on the potential energy surface were determined by additional geometry optimization at the B3LYP/cc-pV(T+d)Z level of theory. Then, harmonic and anharmonic vibrational frequencies and intensities of the minima structures were computed by vibrational perturbation theory (VPT2) at the same level of theory.

III. RESULTS AND DISCUSSION

A. Irradiation experiments in Ar matrix

The band positions of vibrational transitions of the precursor molecule thioacetamide agree well with the literature values.¹⁶ Upon irradiating the matrix with Lyman- α photons, extensive spectral changes occur, and besides the overall decrease of the precursor IR bands, numerous new features also emerge. One of the most prominent among these newly appearing signals is that of thiol tautomers. These are well known to form via UV irradiation of thioacetamide in low-temperature matrices, as was mentioned in Sec. I.^{13,15} Nevertheless, peaks not belonging to any of the thioacetamide tautomers also appear, pointing to the possible formation of photolysis products by destruction of the parent molecule when exposed to UV photons. Most of these previously unidentified IR bands can be assigned when comparing their frequencies with the data found in the literature. For instance, signals with their maxima at 3506.2 and 1980.9 cm⁻¹ can be assigned to the HNCS molecular vibrations [ν (NH) and ν (C=N) stretching modes], respectively.³⁴ Interestingly, no HSCN and HSNC isomers could be observed after

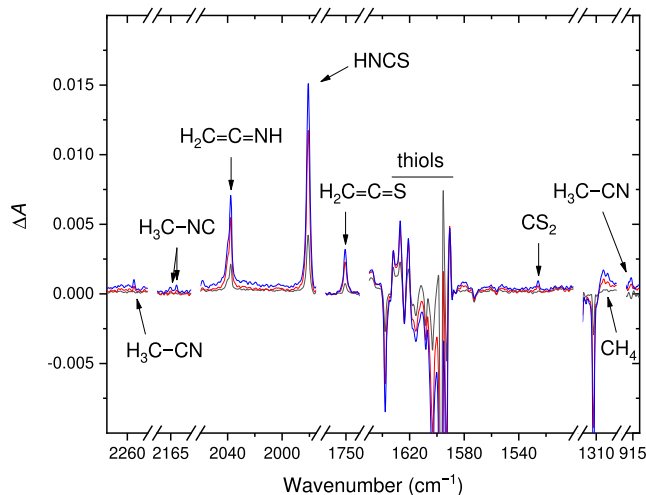


FIG. 2. Temporal evolution of the most prominent bands appearing during exposing thioacetamide to Lyman- α photons isolated in solid Ar after 40 (black trace), 80 (red), and 120 (blue) minutes of photolysis. Negative signals represent bands of the thione tautomer of thioacetamide.

the Lyman- α irradiation, which are well-documented photoisomerization products of HNCS when using longer-wavelength photons.³⁵ It is also possible that even if they form, the utilized Lyman- α photons destroy HSCN and HSNC more efficiently than HNCS. The features at 2256.0 cm⁻¹ [ν (C $\equiv$ N)] and 916.2 cm⁻¹ [ν (CC)] are due to acetonitrile (methyl cyanide, H₃C-CN),³⁶ whereas its isomer methyl isocyanide (H₃C-NC) can be also detected owing to its band at 2160.7 cm⁻¹ [ν (N $\equiv$ C)].³⁶ The presence of ketenimine (H₂C=C=NH) and thioketene (H₂C=C=S) can also be identified through their IR absorption peaks at 2037.7 cm⁻¹ [antisymmetric stretching, ν_{as} (C=C=N)]³⁶ and 1750.7 cm⁻¹ [ν (C=C)],²⁸ respectively. An extremely weak absorption peak of carbon disulfide (CS₂) may be observed at 1526.3 cm⁻¹ [ν_{as} (S=C=S)],³⁷ whereas that of the sulfanyl (or mercapto) radical (SH) at 2606.8 cm⁻¹.²³ Lastly, methane can be found at 1304.9 cm⁻¹ as a broad feature (antisymmetric bending, β_{as}).³⁸

The spectral changes upon photolysis are visualized in Fig. 2; note that they are difference spectra with respect to the spectrum taken at the beginning of the irradiation serving as reference. The assignments done based on the Lyman- α experiments are summarized in Table I. Two extremely weak bands could not be assigned to a vibrational mode of any reasonable molecule or radical; these are features lying at 2229.7 and 2289.6 cm⁻¹.

Similar results were obtained when carrying out consecutive laser UV irradiation (Fig. S1 in the supplementary material). At the wavelengths of 300 and 270 nm, thiol isomers formed exclusively. However, at 240 and 216 nm, the formation of decomposition products can already be monitored although less extensively than during the broadband Lyman- α photolysis. As a result, many bands cannot be observed since they are below the detection limit, such as that of H₃C-CN at 916.2 cm⁻¹ and those of CH₄, CS₂, and H₃C-NC. As for the energetic electron bombardment experiments, the bands of HNCS, H₂C=C=NH, H₂C=C=S, CS₂, and CH₄ can be undoubtedly detected along with those of the thiol tautomers (Fig. S2).

TABLE I. Comparison of the experimental vibrational frequencies and IR intensities of the Lyman- α irradiation products of thioacetamide isolated in solid Ar and in solid *para*-H₂ matrices as well as values taken from literature.

Species	Ar matrix		<i>para</i> -H ₂ matrix		<i>I</i> ^b
	$\tilde{\nu}^a$ (Lit.)	$\tilde{\nu}^a$	$\tilde{\nu}^a$ (Lit.)	$\tilde{\nu}^a$	
HNC	...	...	3628.6 ^c	3628.6	0.529
HNCS	3508.5 ^d	3506.2	[3537.9] ^e	3522.5	0.210
HCN	...	...	3302.9 ^c	3302.9	0.186
CH ₃	...	...	3170.6 ^f	3170.8	0.095
CH ₄	...	...	3025.2, 3016.3, 3008.1 ^g	3026.3, 3017.5, 3009.1	0.223
SH	2607 ^h	2606.8	...	...	...
H ₃ C–CN	2256.2 ⁱ	2256.0	[2266.5] ^j	2262.3	0.039
H ₃ C–NC	2160.6 ⁱ	2165.6, 2160.7	[2166.0] ^j	2163.7	0.028
H ₂ C=C=NH	2037.6 ⁱ	2039.7sh, 2037.7	[2043.58] ^k	2042.4sh, 2040.3	0.264
HNC	...	...	2025.5 ^c	2025.6	0.100
HNCS	1981.8 ^d	1980.9	[1989] ^e	1987.8	1.000
H ₂ C=C=S	1754.6 ^l	1750.7	[1757] ^m	1756.7	0.111
CS ₂	1528.6 ⁿ	1526.3	...	...	...
CH ₃	...	...	1401.7 ^f	1402.3	0.035
CH ₄	1306.0 ^o	1304.9b	1308.3, 1302.9 ^g	1308.4, 1303.5	0.167
NH ₃	...	...	968.07 ^p	968.4	0.276
H ₃ C–CN	916.8 ⁱ	916.2	...	...	...
HCN	...	...	720.6 ^c	720.4	0.184
CH ₃	...	...	624.0 ^f	623.9	0.412

^aIn cm^{−1}.^bIntegrated band areas normalized to that of HNCS at 1987.8 cm^{−1}.^cReference 39.^dReference 34.^eGas-phase value, Ref. 40.^fReference 41.^gReference 42.^hReference 23.ⁱReference 36.^jGas-phase value, Ref. 43.^kGas-phase value, Ref. 44.^lReference 28.^mGas-phase value, Ref. 45.ⁿReference 37.^oReference 38.^pReference 46.

B. Irradiation experiments in *para*-H₂ matrix

Interestingly, the features of the precursor molecule are broader than in Ar, somewhat contradicting what is anticipated, since the spectral bandwidth in *para*-H₂ host is generally less than in any other matrix.¹⁸ However, it is well known that the molecular rotation of small molecules or internal rotation around a single bond in the soft *para*-H₂ matrix is less constrained than in other, more rigid matrices. This rotation, whether internal or molecular, may account for the overall broadening of thioacetamide spectral bands. The qualitative changes in IR spectra when the matrix containing thioacetamide is exposed to Lyman- α photons are similar to those observed in an Ar matrix. It should be noted that there is no literature value for most vibrational frequencies of the decomposition products in low-temperature *para*-H₂. Nonetheless, they can be compared with the Ar-matrix results and gas-

phase literature data, which fundamentally help in their unambiguous identification. It is also worth noting that all peaks are shifted toward larger wavenumbers compared to their positions observed in Ar and shifted to smaller wavenumbers with regard to the gas-phase values, i.e., the frequencies obtained in *para*-H₂ lie between the values taken in Ar and in the gas phase in line with the expectations.

The most prominent features are those of HNCS again at 3522.5 and 1987.8 cm^{−1}, and H₂C=C=NH also has a relatively intense absorption at 2040.3 cm^{−1}. The other decay products that were also detected in Ar show less strong signals, at 2262.3 (H₃C–CN), 2163.7 (H₃C–NC), and 1756.7 cm^{−1} (H₂C=C=S), respectively. The different rotational transitions of the degenerate β_{as} vibration of CH₄ at 1308.4 and 1303.5 cm^{−1} can also be detected. Furthermore, some features were observed at 3026.3, 3017.5, and 3009.1 cm^{−1}, which

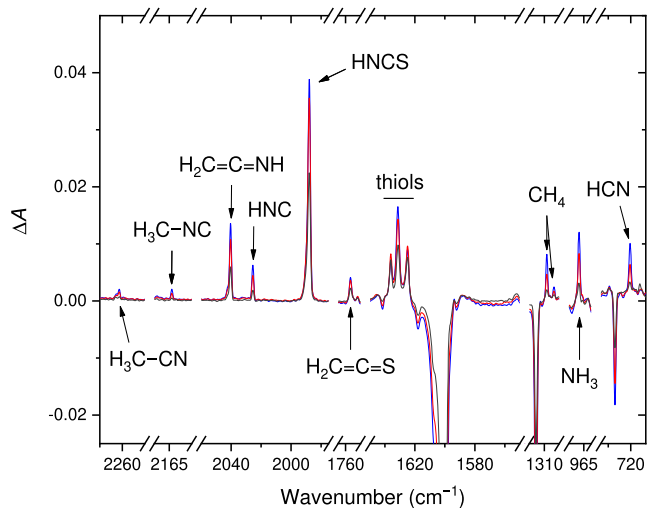


FIG. 3. Temporal evolution of the most prominent bands appearing when exposing thioacetamide to Lyman- α photons isolated in solid *para*-H₂ after 40 (black trace), 80 (red), and 120 (blue) minutes of photolysis. Negative signals represent bands of the thione tautomer of thioacetamide.

are attributed to the ν_{as} vibrational mode of CH₄ coupled with various rotational transitions.⁴² These features are absent in Ar matrix. Moreover, new absorption peaks belonging to species not seen in Ar also emerge; these are those of hydrogen cyanide (HCN) at 3302.9 and 720.4 cm⁻¹ [$\nu(\text{CH})$ and $\beta(\text{HCN})$],³⁹ hydrogen isocyanide (HNC) at 3628.6 and 2025.6 cm⁻¹ [$\nu(\text{NH})$ and $\nu(\text{N}=\text{C})$],³⁹ methyl radical (CH₃) at 3170.8, 1402.3, and 623.9 cm⁻¹ [$\nu(\text{CH})$, $\beta_{as}(\text{CH}_3)$, and the out-of-plane bending $\beta_{op}(\text{CH}_3)$],⁴¹ and ammonia (NH₃) at 968.4 cm⁻¹ (the symmetric bending mode, β_s),⁴⁶ respectively. The appearance of these small molecules, and especially the reactive CH₃ radical, is likely caused by the host material; it is well known that the soft *para*-H₂ matrix allows for facile diffusion of small molecules or molecular fragments; thus, when the parent molecule dissociates, they can swiftly move apart from each other before recombining.¹⁸ This is in contrast with what happens in the more rigid Ar matrix, where the stronger cage effect enhances the possibility of recombination or complex formation and therefore reduces the overall efficiency of photodissociation. The lack of CS₂ in *para*-H₂ matrix after irradiation may be explained by the fact that *para*-H₂ matrices are generally more dilute than the traditional ones, as the formation of CS₂ requires two neighboring precursor molecules; thus, dimers must have been present in Ar matrix after deposition. Similar to Ar matrix, several bands could not be assigned in *para*-H₂; nevertheless, their kinetics show similarities with those of the products listed above. The changes upon Lyman- α photolysis are plotted in Fig. 3, note that they are difference spectra with the spectrum taken at the beginning of the irradiation used as reference. The obtained vibrational frequencies of the irradiation products are summarized in Table I as well.

The laser UV photolysis experiments yield similar results with very similar peak heights (Fig. S3). HNCS is an exception, however, for which the absorption strength is found to be significantly higher

than after the Lyman- α irradiation is finished, pointing to a relatively more efficient formation.

In contrast, the optical quality of the matrix deteriorated to a great extent upon the 5 keV electron irradiation and started scattering, resulting in an increase in the baseline and more difficult interpretation of the spectra (Fig. S4). This worsening of optical quality of the matrix may be attributed to the formation of “hot species” due to the simultaneous deposition/irradiation and their deposition on the substrate, resulting in annealing of the matrix. Still, the presence of HNCS, H₂C=C=NH, CH₄, and likely H₂C=C=S can be proven.

C. Kinetics of the Lyman- α photolysis in *para*-H₂ matrix

As already discussed in Sec. III B, when the sample is exposed to Lyman- α photons, fundamental changes can be observed throughout the MIR spectrum of the sample. Briefly, in parallel to the decomposition of the precursor thioacetamide, numerous bands of the photolytic products emerge. In this section, we aim to determine their mixing ratios as well as their kinetic behavior upon irradiation. The kinetic curves can be simply obtained by integrating the band areas of the peaks of a respective species and plotting them against the irradiation time. However, these curves do not consider the differing absorption coefficients of bands belonging to different vibrational modes. Therefore, the integrated band areas must be normalized first. One frequently used approach is to calculate the mixing ratios of the molecules with respect to the host matrix, which can be done for a *para*-H₂ host¹⁸ and has been utilized by our group on many occasions, e.g., Ref. 21. Basically, the integrated band areas of the vibrational bands of each species were normalized by their corresponding computed anharmonic IR intensities and the optical path length of the spectrometer IR beam in the sample. The optical path length (in cm⁻¹) can be determined by integrating the band areas of the Q1(0) + S0(0) and the S1(0) + S0(0) transitions of *para*-H₂ in the 4520–4495 and 4855–4825 cm⁻¹ regions using the coefficients 90 ± 2 and 7.0 ± 0.2 cm⁻², respectively.¹⁸ The matrix thickness can also be estimated from the optical path lengths by taking into account the incidence angle of the spectrometer beam ($\approx 60^\circ$ to the surface normal of the substrate), yielding ≈ 0.03 mm as a result. As for the measurements done in Ar, the optical paths could not be calculated since the He–Ne laser interferometry system had not been installed; however, the column density of each species (in cm⁻²) can be calculated based on a modified Lambert–Beer formula introduced in the work of Bennett *et al.*⁴⁷ It should be noted that the column densities acquired in the two different matrix environments can be directly compared: The mixing ratios obtained for *para*-H₂ matrices can be converted to column densities. For this, the values in ppm have to be divided by 10^6 (because of the ppm scale), by 23.16 (molar volume of *para*-H₂ in cm³ mol⁻¹), and by 2 (accounting for the fact that the beam travels twice through the sample before and after the reflection on the substrate surface), and then they must be multiplied by 0.0168 or 0.0186 (optical lengths in cm obtained in the Lyman- α and the laser UV photolysis experiments, respectively), by Avogadro’s number, and by the cosine of 60° (incident angle of the IR beam with regard to the surface normal of the substrate). This yields a conversion factor in the order of 1×10^{14} cm⁻².

When it was possible, multiple peaks were considered for a given species and the calculated mixing ratios were averaged. It is worth noting that the values obtained from the different vibrational modes of the same molecule also give an estimate on the quality of the computed intensities. In the case of the precursor thioacetamide, the bands at 1599.9 and 1350.7 cm^{-1} were used, which are due to the βNH_2 and νCN modes being the two bands of the molecule with the strongest absorption; the used computed anharmonic intensities were 127 and 200 km mol^{-1} . For the HNCS molecule, both observed bands were utilized (i.e., at 3522.5 and 1987.8 cm^{-1}), taking 206 and 658 km mol^{-1} , respectively, as their IR absorption coefficients. The same applies to CH_4 (79.7 and 37.2 km mol^{-1} for its $\nu_{\text{as}}\text{CH}$ and the $\beta_{\text{as}}\text{CH}_4$ modes, respectively), HNC (229 and 58.1 km mol^{-1} for the bands at 3628.6 and 2025.6 cm^{-1} , respectively), and HCN (62.2 and 38.2 km mol^{-1} for the bands at 3302.9 and 720.4 cm^{-1} , respectively). Two of the three observed bands of CH_3 radical were considered (15.8 and 6.4 km mol^{-1} for the 3170.8 and 1402.3 cm^{-1} bands, respectively). The rest of the photolysis products had only one band, which could be used for determining the kinetic curves; these are 323 km mol^{-1} (2040.3 cm^{-1} , $\text{H}_2\text{C}=\text{C}=\text{NH}$), 9.3 km mol^{-1} (2262.3 cm^{-1} , $\text{H}_3\text{C}-\text{CN}$), 127 km mol^{-1} (2163.7 cm^{-1} , $\text{H}_3\text{C}-\text{NC}$), 385 km mol^{-1} (1756.7 cm^{-1} , $\text{H}_2\text{C}=\text{C}=\text{S}$), and 145 km mol^{-1} (968.4 cm^{-1} , NH_3). The mixing ratio of the tautomers was also calculated using three bands of the **aC** thiol at 1038.2 cm^{-1} (77 km mol^{-1}), 992.3 cm^{-1} (38 km mol^{-1}), and 819.5 cm^{-1} (83 km mol^{-1}), one

band of the **aT** thiol at 1625.3 cm^{-1} (145 km mol^{-1}), two bands of the **sC** thiol at 1240.2 cm^{-1} (74 km mol^{-1}) and 1257.5 cm^{-1} (107 km mol^{-1}), and one of the **sT** thiol at 1270.1 cm^{-1} (244 km mol^{-1}), respectively. The IR absorption coefficients of the thiol isomers are theoretical values corrected based on experimental results and were taken from our earlier work along with the notations **aC**, **aT**, **sC**, and **sT**.¹⁶ In order to obtain the column densities for the experiments carried out in Ar matrices, the same bands were used as detailed above.

By having a look at the produced curves (Fig. 4), one can classify the irradiation products into four groups based on their qualitative kinetic behavior: The first group consists of thiol tautomers, unsurprisingly, they form at the earliest stage of the photolysis by the well-known rapid H atom migration from the $-\text{NH}_2$ moiety to the sulfur atom upon energetic radiation.¹³ Their presence is obvious throughout the irradiation, although their mixing ratio stops growing after reaching a certain point and becomes nearly constant or even slightly decreasing, i.e., their formation and destruction rates become more or less equal. The primary degradation products, such as HNCS, $\text{H}_2\text{C}=\text{C}=\text{NH}$, and $\text{H}_2\text{C}=\text{C}=\text{S}$, also appear swiftly; their initial formation rate is comparable to those of the first group and apparently higher than those of the other product molecules. Among them, the most abundant HNCS seemingly reaches a plateau after some 100 min of sample exposure to Lyman- α photons. The next group of three molecules, CH_3 , NH_3 , and $\text{H}_3\text{C}-\text{CN}$ have different,

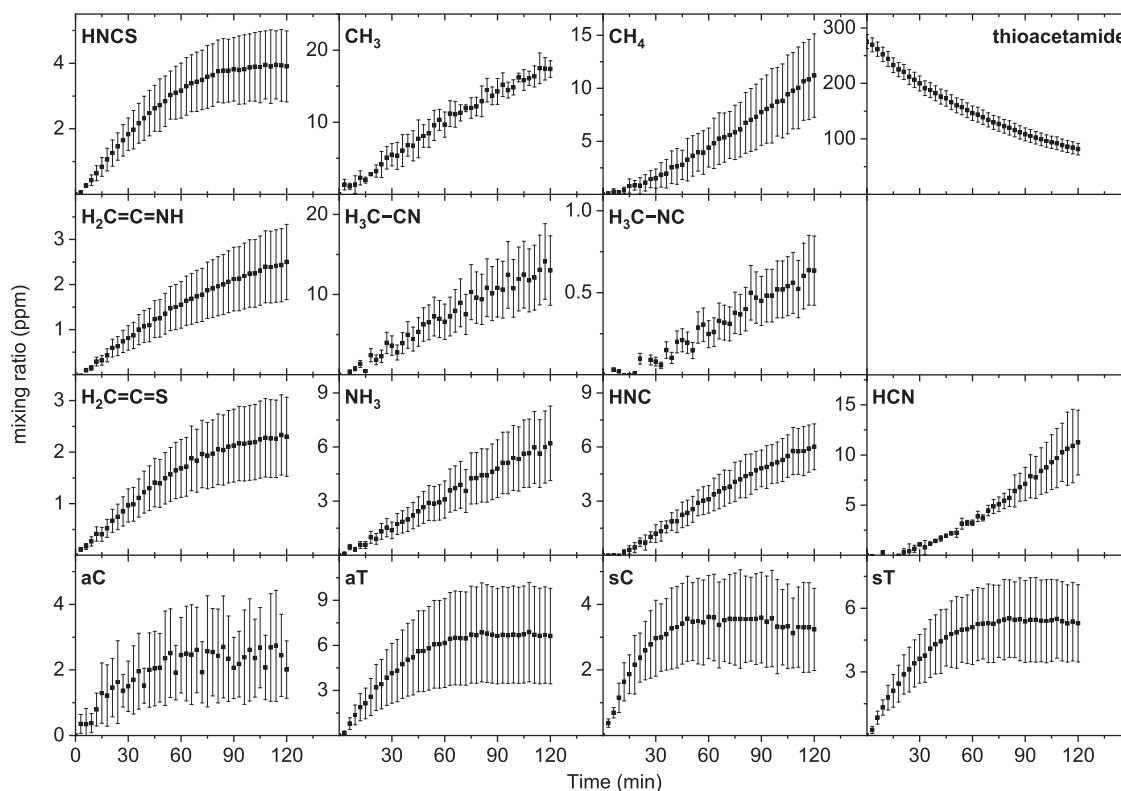


FIG. 4. Kinetic curves of the precursor and the products during Lyman- α photolysis in a *para*- H_2 matrix. See details in the main text.

linear-like kinetic curves, suggesting their participation in a complex formation/destruction mechanism, which may result in the apparent lower initial formation rate than observed for the second molecular group. The members of the fourth group show kinetic curves where the formation only starts after a shorter or longer initial period depending on the molecule, these are in order CH_4 , $\text{H}_3\text{C}-\text{NC}$, HNC , and HCN . This feature implies the necessity of the accumulation of some other (primary) irradiation products first suggesting that these species may be secondary products. Nevertheless, none of the curves of the products show first-order kinetic behavior (i.e., they cannot be fitted with simple single exponential functions), pointing to a complex reaction mechanism involving the simultaneous formation/degradation of all species, which would require the solution of a set of coupled differential equations. In contrast, the abundant precursor nicely follows a (pseudo)-first-order decay with an approximate half-life of 58 min owing to the fact that it is in large excess in comparison with the daughter species during the time of irradiation. Similar phenomena can be observed when inspecting the kinetic plots obtained in Ar matrix and the products may be divided into three groups (Fig. S5): The thiol conformers comprise the first group, reaching a saturation point after some 60 min of irradiation, whereas the primary products HNCS , $\text{H}_2\text{C}=\text{C}=\text{NH}$, and $\text{H}_2\text{C}=\text{C}=\text{S}$ display a monotonic growth during the whole irradiation. The rest of the molecules have kinetic curves with an initial phase, during

which no formation can be observed, pointing to the necessity for the accumulation of other species before their mixing ratio may start growing. The required species may be CH_3 in the case of CH_4 , but unlike in *para*- H_2 , the former cannot be detected in Ar. The other two species ($\text{H}_3\text{C}-\text{CN}$ and $\text{H}_3\text{C}-\text{NC}$) are isomers of $\text{H}_2\text{C}=\text{C}=\text{NH}$; therefore, they may necessitate the accumulation of the latter before they can start forming.

D. Kinetics of laser UV photolysis in *para*- H_2 matrix

Figure 5 shows the resulting kinetic curves of the precursor, the thiol tautomers, and the products upon 216 nm laser UV photolysis. This wavelength was selected to be visualized since its use resulted in the highest consumption rate of the precursor and formation rate of the product molecules. After ≈ 30 min, the irradiation was stopped to remove the collimating lens and after that, the laser beam became fully focused on the sample, leading to an evident acceleration of precursor degradation and the formation of product molecules. The kinetics shows some similarities with the one obtained during the Lyman- α irradiation study discussed in Sec. III C although there are significant differences. The first group is made up of thiols, which quickly form even in the first 30 min of the irradiation when the collimating lens was used, meaning lower photon fluxes. Then, during the second 30 min, *aT* and *sC* even start decaying whereas *sT*

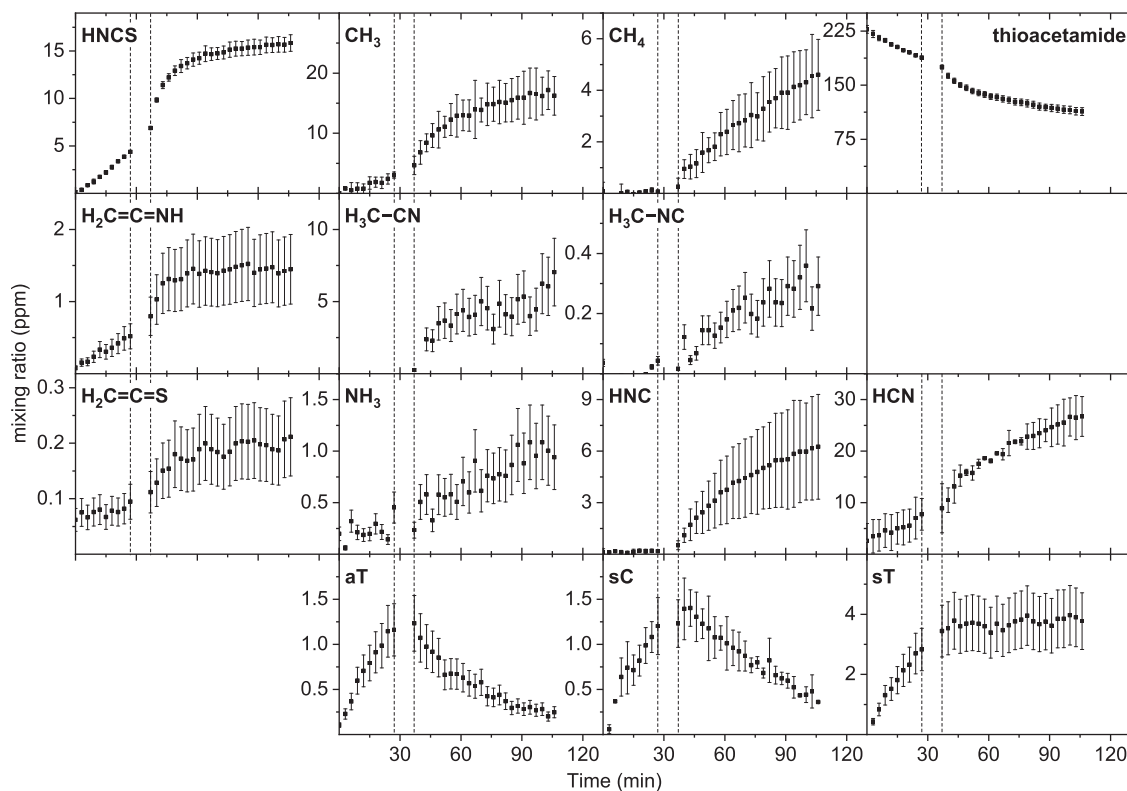


FIG. 5. Kinetic curves of the precursor and the products during the 216 nm UV laser photolysis in a *para*- H_2 matrix. The vertical dashed lines mark the time period when the UV photolysis was paused. See details in the main text.

reaches a (quasi-)stationary state. In group II, HNCS, $\text{H}_2\text{C}=\text{C}=\text{NH}$, and $\text{H}_2\text{C}=\text{C}=\text{S}$ also appear in the first 30 min of photolysis, however, at a lower rate than thiols; in the second part of the photolysis, their apparent formation rate gradually decreases to nearly zero. Finally, the remaining photolysis products show various kinetic behavior, and classification based on their apparent kinetic profiles is dubious. In Ar matrix, the thiols readily form during the 240 nm laser irradiation and it is evident from the kinetic plots that the temporal evolution of the mixing ratio of the thiol conformers shows great variability (Fig. S6): The mixing ratios of the **aT** and **aC** conformers decrease, whereas those of **sC** and **sT** show an increasing trend at 240 nm. In contrast to this, **aT** and **sC** start decomposing at 216 nm but **aC** and **sT** show resistance against the UV photons at this wavelength. The remaining molecules show monotonic growth independent of the applied laser wavelength. Nevertheless, HNCS should be highlighted as its formation rate becomes significantly higher at the shorter wavelength used, which does not hold true for the other three species, $\text{H}_2\text{C}=\text{C}=\text{NH}$, $\text{H}_3\text{C}-\text{CN}$, and $\text{H}_2\text{C}=\text{C}=\text{S}$, respectively.

E. Molar balance of the photolysis studies in *para*- H_2 matrices

Determination of the mixing ratios also allows for predicting the molar balance of the radiolytic processes (Table II). The amount of decomposed precursor is estimated to be 200 and 161 ppm for the Lyman- α and the 216 nm laser UV photolysis experiments, respectively. The most abundant products are the CH_3 , CH_4 , $\text{H}_3\text{C}-\text{CN}$, and HCN upon exposure of the sample to Lyman- α photons, since they all have a mixing ratio higher than 10 ppm. The same holds true for HNCS when carrying out the 216 nm laser UV photolysis study. The aggregated abundance of thiols also exceeds 10 ppm in the former case. The other decay products are less abundant, with most of them having a mixing ratio between 1 and 10 ppm; these are (in decreasing order) NH_3 , HNC, HNCS, $\text{H}_2\text{C}=\text{C}=\text{NH}$, $\text{H}_2\text{C}=\text{C}=\text{S}$, and finally, $\text{H}_3\text{C}-\text{NC}$ upon Lyman- α irradiation. The same order when exposing the sample to 216 nm photons is $\text{H}_3\text{C}-\text{CN}$, HNC, CH_4 , $\text{H}_2\text{C}=\text{C}=\text{NH}$, NH_3 , $\text{H}_3\text{C}-\text{NC}$, and $\text{H}_2\text{C}=\text{C}=\text{S}$. As far as the two radiation sources are concerned, the abundance of each species is more or less comparable to each other, i.e., they differ from each other by no more than a factor of 2–5 by the end of irradiation. The only significant difference, when the mixing ratios differ from each other by more than an order of magnitude, can be found for some thiols, namely, **aC** and **aT**; **sC** may also be listed in this category even though the factor in its case is slightly less than 10. The mixing ratio data also point to the somewhat more selective nature of laser photolysis, most likely owing to its monochromatic nature and the applied wavelength, with a preference toward HNCS formation and suppression of the formation of other products. This is in contrast to the findings of the broadband Lyman- α irradiation, where all reaction channels may be open, simultaneously resulting in the lack of a preferred pathway. By having a look at the element-specific balances, one can see that in the case of C and N, the abundances of decomposition products account for roughly 30% of the decomposed precursor molecules in both cases, whereas this value drops to ~10% for S atoms. The possible cause for the balances being lower than 100% includes numerous factors involving the uncertainty of the computed IR intensities or errors in the

TABLE II. Change in mixing ratios (in ppm) of the precursor and the products during photolysis and the molar balance.

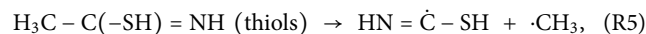
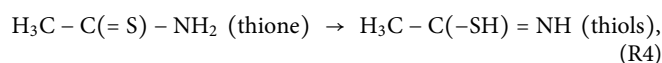
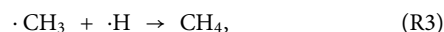
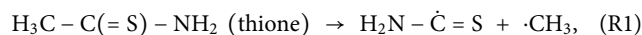
Species	Δ mixing ratio	
	Lyman- α	Laser UV
Thioacetamide	-200 ± 30	-161 ± 8
HNCS	4 ± 1	15.7 ± 0.7
CH_3	19 ± 2	17 ± 2
CH_4	11 ± 4	4.6 ± 0.9
$\text{H}_2\text{C}=\text{C}=\text{NH}$	2.5 ± 0.9	1.3 ± 0.4
$\text{H}_3\text{C}-\text{CN}$	13 ± 5	7 ± 2
$\text{H}_3\text{C}-\text{NC}$	0.7 ± 0.2	0.28 ± 0.08
$\text{H}_2\text{C}=\text{C}=\text{S}$	0.9 ± 0.3	0.15 ± 0.04
NH_3	6 ± 2	0.8 ± 0.2
HNC	6 ± 1	6 ± 2
HCN	12 ± 4	24 ± 5
aC	2 ± 1	...
aT	7 ± 3	0.16 ± 0.04
sC	3 ± 1	0.43 ± 0.01
sT	5 ± 2	4 ± 1
C balance ^a	$(33 \pm 12)\%$	$(29 \pm 8)\%$
S balance	$(11 \pm 6)\%$	$(13 \pm 2)\%$
N balance	$(31 \pm 16)\%$	$(37 \pm 9)\%$

^aWhen calculating the C balance, it has to be taken into account that the precursor as well as some photoproducts contain two C atoms.

integrated band areas (especially the weak ones). The apparent preferential depletion of S is due to non-detection of the important photoproduct H_2S .

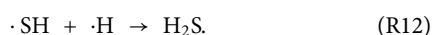
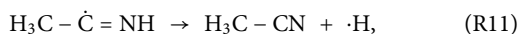
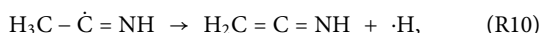
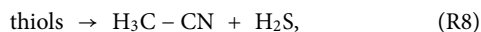
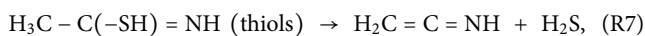
F. Decomposition mechanism

Using the experimentally obtained temporal profiles of the mixing ratios, some suggestions can also be made for the decomposition mechanism when thioacetamide is exposed to energetic radiation. Three main primary decomposition pathways may be hypothesized using chemical intuition as discussed below. The radical centers are marked in each case and the structure of the thione and thiol tautomers of thioacetamide are denoted in this section for the sake of easier interpretation. We have

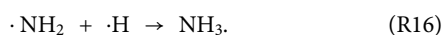
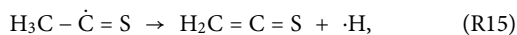
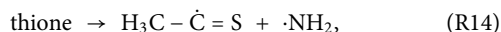
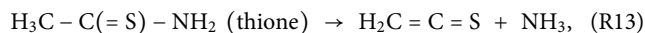


Accordingly, HNCS may form through two reaction channels: elimination of the methyl group ($-\text{CH}_3$) on the thione [reaction (R1)] or the thiol [reaction (R5)] tautomers after the rapid tautomerization of the thione precursor involving the H atom

migration from the amino ($-\text{NH}_2$) group to the sulfur atom [reaction (R4)]. The $\cdot\text{CH}_3$ radical may react with a neighboring H atom, leading to the formation of a stable CH_4 molecule [reaction (R3)]. The other transient molecules $\text{H}_2\text{N}-\dot{\text{C}}=\text{S}$ [reaction (R1)] and $\text{HN}=\dot{\text{C}}-\text{SH}$ [reaction (R5)] may decompose into HNCS following reactions (R2) and (R6), respectively. It is important to note that neither $\text{H}_2\text{N}-\dot{\text{C}}=\text{S}$ nor $\text{HN}=\dot{\text{C}}-\text{SH}$ was directly observed in our irradiated samples. Moreover, according to the reactions listed above, one would expect that the amount of HNCS should be approximately equal to the sum of the mixing ratios of $\cdot\text{CH}_3$ and CH_4 , which holds true for the 216 nm laser UV photolysis (Table II). The apparent discrepancy upon Lyman- α irradiation may be due to undetectable sulfurous species (e.g., $\text{H}_2\text{N}-\dot{\text{C}}=\text{S}$, $\text{HN}=\dot{\text{C}}-\text{SH}$, or even S atoms), further decomposition of HNCS, alternative formation pathways of $\cdot\text{CH}_3$ and CH_4 (for instance, $\cdot\text{CH}_3$ from the decay of $\text{H}_3\text{C}-\dot{\text{C}}\text{N}$ or $\text{H}_3\text{C}-\text{NC}$, see below), or because of uncertainty in the computed IR intensities. Since there is no significant difference between the mixing ratios of $\cdot\text{CH}_3$ and CH_4 after the Lyman- α and the 216 nm laser UV photolysis but the amount of HNCS decreases by a factor of four in the former case, the importance of an efficient HNCS decomposition channel is suggested from the above-listed possibilities. We have



Another possibility is the elimination of H_2S and direct formation of either $\text{H}_2\text{C}=\text{C}=\text{NH}$ [reaction (R7)] or $\text{H}_3\text{C}-\text{CN}$ [reaction (R8)]. Alternatively, after cleavage of the C-S bond in the thiol molecule, $\cdot\text{SH}$ radical could also be formed [reaction (R9)], which was observed in Ar matrices. The other product, $\text{H}_3\text{C}-\dot{\text{C}}=\text{NH}$ radical, may lose an H atom, yielding either $\text{H}_2\text{C}=\text{C}=\text{NH}$ [reaction (R10)] or $\text{H}_3\text{C}-\text{CN}$ [reaction (R11)], serving as an indirect route for their formation. Finally, $\cdot\text{SH}$ can also react with an H atom further to hydrogen sulfide [H_2S , reaction (R12)]. Unfortunately, both $\cdot\text{SH}$ and H_2S have extremely weak absorption peaks, making their doubtless identification not possible in *para*- H_2 (the IR intensities of the $\nu(\text{S}-\text{H})$ mode of both species are computed to be in the order of 1 km mol^{-1}). Furthermore, H_2S exhibits a complex, broad band with multiple peaks in the Ar matrix (e.g., Ref. 23), rendering its observation even more difficult. Lastly, thiols also absorb in this region due to their S-H moieties,¹⁶ possibly overlapping with the vibrational bands of both H_2S and SH . We have

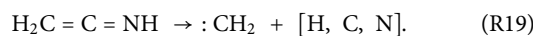
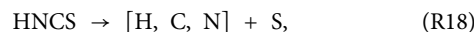


The third possible pathway is the loss of amino group ($-\text{NH}_2$) from the thione tautomeric form, yielding $\text{H}_2\text{C}=\text{C}=\text{S}$ [reaction (R13)]. The indirect pathway is also a viable one [reactions (R14) and (R15)], where the other decay product amidogen radical ($\cdot\text{NH}_2$) was not detected in the matrix but its stable hydrogenation product NH_3 was [reaction (R16)]. The lack of NH_3 detection in Ar implies the radical pathway proposed in reactions (R14) and (R15).

Reactions (R1)–(R16) explain the presence of seven decay products out of the ten listed in Table II. The remaining species may form through secondary reactions, such as the already-known photoisomerization of $\text{H}_2\text{C}=\text{C}=\text{NH}$ to its isomer $\text{H}_3\text{C}-\text{CN}$ and eventually to $\text{H}_3\text{C}-\text{NC}$, creating a photoequilibrium between them [reaction (R17)],³⁶ which may explain their similar relative quantities after prolonged Lyman- α and laser UV photolysis (Table II). We have



whereas the other two species, HNC and HCN (treated together as [H, C, N]), may result from multiple reactions, such as photodegradation of HNCS or $\text{H}_2\text{C}=\text{C}=\text{NH}$, respectively [reactions (R18) and (R19)].^{36,48} It should be noted, however, that according to the authors of the work of Krupa *et al.*,⁴⁸ only the formation of $\text{HCN} \cdots \text{S}$ complex and not that of $\text{HNC} \cdots \text{S}$ or the monomeric forms can be observed when photolyzing HNCS in Ar matrices, suggesting that the HNC formation is preferred via reaction (R19).³⁶ It must be noted, however, that they used longer-wavelength photons (from 289 to 225 nm) and the photolytic response upon Lyman- α irradiation may be different: The formation of $\text{HNC} \cdots \text{S}$ may be preferred over that of $\text{HCN} \cdots \text{S}$. Nonetheless, should any of the two complexes form, they are then expected not to be stable in the soft *para*- H_2 matrix, allowing for their breakup and thus the detection of monomeric [H, C, N]. Moreover, the interconversion between the [H, C, N] isomers can also be anticipated upon energetic VUV irradiation,⁴⁹ further complicating the possible reaction mechanism. It is also worth noting that no evidence for the presence of the above-mentioned complexes was found in the Ar-matrix experiments, either. We have



The sulfur atoms, provided that they form via reaction (R18), are IR inactive and thus cannot be observed but they are expected to participate in an efficient hydrogenation reaction in an H-rich environment, giving rise to $\cdot\text{SH}$ and eventually H_2S . The methylene radical ($\cdot\text{CH}_2$) forming in reaction (R19) is also likely to be hydrogenated consecutively in a *para*- H_2 environment to $\cdot\text{CH}_3$ and eventually to CH_4 . The constant depletion of $\text{H}_2\text{C}=\text{C}=\text{NH}$ via reaction (R19) can also induce a shift in the equilibrium described in reaction (R17) toward the left so that $\text{H}_3\text{C}-\text{CN}$ (and eventually $\text{H}_3\text{C}-\text{NC}$) converts back to $\text{H}_2\text{C}=\text{C}=\text{NH}$. $\text{H}_3\text{C}-\text{NC}$ may also further isomerize to the zwitterionic $\text{H}_2\text{C}=\text{N}^+-\text{CH}^-$,⁵⁰ which latter could decompose into [H, C, N] and $\cdot\text{CH}_2$; however, no spectroscopic evidence could be found for its existence in the matrix.

The kinetics of the listed species qualitatively supports the reaction mechanism detailed above (see Secs. III C and III D); based on the appearance of the kinetic curves, HNCS, $\text{H}_2\text{C}=\text{C}=\text{NH}$, and $\text{H}_2\text{C}=\text{C}=\text{S}$ are all primary products forming at a somewhat lower rate than the thiol tautomers. The decomposition of HNCS according to reaction (R18) becomes gradually important once its mixing ratio reaches levels sufficient enough to produce the secondary product $[\text{H}, \text{C}, \text{N}]$ isomers, similar to $\text{H}_2\text{C}=\text{C}=\text{NH}$ [reaction (R19)]. The latter also photoisomerizes into its isomers via reaction (R17), which are secondary products based on their kinetic curves, and their formation starts only after a transitional period. Reactions (R1), (R5), and (R13) yield $\cdot\text{CH}_3$ and NH_3 ; respectively, however, they can either transform into secondary products (e.g., reaction (R3) for $\cdot\text{CH}_3$) or be formed indirectly [reaction (R16) for NH_3], thus complicating overall reaction scheme. Evidently, the lower formation rate of $\text{CH}_3\text{--NC}$ than $\text{CH}_3\text{--CN}$ can be explained by the fact that the former forms from the latter [reaction (R17)]; the same applies to the $\text{CH}_4\text{--CH}_3$ binary [reaction (R3)]. Similar conclusions can be drawn from the kinetic curves of the 216 nm laser UV photolysis as well, with one exception. Here, the formation of HCN seems to be preferred to that of HNC. One explanation could be that, in line with the findings presented in the work of Krupa *et al.*,⁴⁸ the formation of $\text{HCN}\cdot\cdot\text{S}$ (and eventually HCN in *para*- H_2 matrix) is more efficient than that of $\text{HNC}\cdot\cdot\text{S}$ (eventually HNC) when HNCS breaks apart and the HCN to HNC conversion becomes important only upon Lyman- α photolysis. The scarcity and quality of data obtained upon energetic electron bombardment do not allow us to draw any conclusion with regard to the decomposition mechanism when this type of radiation source is used. Even so, it is expected to be similar to those observable upon Lyman- α or laser UV photolysis.

IV. CONCLUSION

The photolytic study of a sulfurous compound, thioacetamide, was carried out in Ar and in the quantum solid *para*- H_2 matrices. Three different types of radiation sources were utilized in separate experiments: a microwave discharge H atom lamp providing Lyman- α photons, a UV laser setup producing 300, 270, 240, and 216 nm photons, and an electron gun emitting 5 keV electrons. These measurements generated results that enable us to draw conclusions about how the matrix environment and the type and energy of radiation affect the outcome.

Upon energetic irradiation, the already well-described tautomerization of the most stable thione form to the higher-energy thiol isomers can be observed. In addition, decomposition of the precursor into numerous irradiation product species is evident in every experiment, independent of the matrix environment or the type of radiation. As far as influence of the matrix on decomposition pathways is concerned, the generally more rigid Ar matrix prevents the migration of decay products from each other, enhancing the possibility of recombination of radicals and thus reducing the overall efficiency of irradiation. In contrast, the diminished cage effect in *para*- H_2 matrix allows for the diffusion of small species and thus their detection also, resulting in increased decay rate of the precursor molecule. As for the different radiation sources, all of them yielded similar qualitative results with respect to the decay products, i.e., the reactions run on the same channels in all cases. Nevertheless,

slight differences can be observed from the quantitative point of view; the amount of species varies depending on the radiation, suggesting the preference for different reaction pathways in each case. Electron bombardment in parallel with deposition is a less ideal choice compared to photolysis, as far as matrix isolation is concerned, as it induces a significant worsening of the optical quality of the matrix.

Based on the temporal evolution of species and chemical intuition, some aspects of the reaction mechanism can be proposed. Apparently, the HNCS formation is one of the two more important ones along with the initial elimination of CH_3 . The other important decomposition channel is that an H_2S molecule leaves the thiol tautomeric form, which comes along with the formation of one of the two $\text{C}_2\text{H}_3\text{N}$ isomers: $\text{H}_2\text{C}=\text{C}=\text{NH}$ or $\text{H}_3\text{C--CN}$. The relative dominance of these two channels depends on the radiation source used, which may affect them either directly or indirectly (through influencing the secondary reactions). The least important channel is the one that involves the production of NH_3 and $\text{H}_2\text{C}=\text{C}=\text{S}$. Several secondary products could also be observed, especially, in the later stages of photolysis. The third $\text{C}_2\text{H}_3\text{N}$ isomer, $\text{H}_3\text{C--NC}$, likely forms through the isomerization of $\text{H}_3\text{C--CN}$, whereas the small molecules HNC and HCN should originate from decomposition of HNCS or $\text{H}_2\text{C}=\text{C}=\text{NH}$. The importance of photoisomerization between the $[\text{H}, \text{C}, \text{N}]$ isomers cannot be ruled out either.

Some of the listed species have already been detected in the ISM, making the findings of this work even more relevant from an astrophysical point of view. HNCS is one of them, detected in Sgr B2 through its millimeter-wave spectral lines back in the late 1970s.⁵¹ The other products of this decomposition channel have also been observed already in Sgr A* by its Q branch at 16.5 μm and R(0) line at 16.0 μm (CH_3)⁵² and in NGC 7538 IRS 9 based on its absorption at 7.6 μm (CH_4).⁵³ Although there is no proof for the existence of $\text{H}_2\text{C}=\text{C}=\text{NH}$ and $\text{H}_3\text{C--NC}$ in the ISM currently, there is for the third isomer $\text{H}_3\text{C--CN}$ along with the respective elimination products SH and H_2S .^{54–56} The species forming via the third reaction pathway, $\text{H}_2\text{C}=\text{C}=\text{S}$ as well as NH_3 , are also evident in space.^{57,58} Lastly, the presence of HNC and HCN in interstellar environments has been known for decades.^{59–63}

The decomposition channels revealed by this study will help future irradiation experiments to be carried out with the astrophysically more relevant thioacetamide ice, which is expected to be a more complex environment with more ambiguous results due to the general broadening of spectral bands as a consequence of extensive interactions in the matter. In addition, the spectral information of all the species provided by experiments will also be of help when identifying them in *para*- H_2 matrices in future studies. Furthermore, these degradation pathways may also be important in space environments, suggesting that thioacetamide can only survive in the core of dense molecular clouds shielded from energetic radiation and the observation of degradation products of this study may indirectly indicate its presence in the ISM.

SUPPLEMENTARY MATERIAL

The supplementary material for this article includes the following: (Figures S1 and S3) temporal evolution of the most prominent bands appearing when exposing thioacetamide to 216 nm laser UV

photons isolated in solid Ar and in *para*-H₂; (Figures S2 and S4) difference spectrum of the most prominent bands appearing after exposing thioacetamide to 5 keV electrons isolated in solid Ar and in *para*-H₂ with respect to blank experiment; and (Figures S5 and S6) Kinetic curves of the precursor as well as the products during the Lyman- α photolysis and during the subsequent 240 and 216 nm UV laser photolyses in Ar matrices.

ACKNOWLEDGMENTS

The authors would like to thank the Hungarian Academy of Sciences for funding this research through the Lendület program. They also thank the Hungarian Scientific Research Fund (Grant No. OTKA K143196) and the Institutional Excellence Program of the Eötvös Loránd University (Grant No. TKP2020-IKA-05). S.G. was supported by the “Bolyai-ösztöndíj” of the Hungarian Academy of Sciences. B.K. was supported by the “ÚNKP-22-3 New National Excellence Program” of the Ministry for Innovation and Technology from the source of the National Research, Development and Innovation Fund. The authors are grateful for and would like to thank an anonymous referee for significantly contributing to the improvement of the manuscript during the revision process.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Sándor Góbi: Conceptualization (lead); Formal analysis (lead); Funding acquisition (supporting); Investigation (lead); Methodology (lead); Project administration (equal); Supervision (equal); Validation (lead); Visualization (lead); Writing – original draft (lead). **Barbara Keresztes:** Investigation (supporting); Writing – review & editing (supporting). **Anita Schneiker:** Investigation (supporting); Writing – review & editing (supporting). **Gopi Ragupathy:** Investigation (supporting); Writing – review & editing (supporting). **György Tarczay:** Funding acquisition (lead); Project administration (equal); Resources (lead); Supervision (equal); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

- 1 D. E. Anderson, E. A. Bergin, S. Maret, and V. Wakelam, “New constraints on the sulfur reservoir in the dense interstellar medium provided by spitzer observations of S_I in shocked gas,” *Astrophys. J.* **779**, 141 (2013).
- 2 M. Kama, O. Shorttle, A. S. Jermyn, C. P. Folsom, K. Furuya, E. A. Bergin, C. Walsh, and L. Keller, “Abundant refractory sulfur in protoplanetary disks,” *Astrophys. J.* **885**, 114 (2019).
- 3 D. V. Mifsud, Z. Kaňuchová, P. Herczku, S. Ioppolo, Z. Juhász, S. T. S. Kovács, N. J. Mason, R. W. McCullough, and B. Sulik, “Sulfur ice astrochemistry: A review of laboratory studies,” *Space Sci. Rev.* **217**, 14 (2021).

- 4 T. H. Vidal, J. C. Loison, A. Y. Jaziri, M. Ruaud, P. Gratier, and V. Wakelam, “On the reservoir of sulphur in dark clouds: Chemistry and elemental abundance reconciled,” *Mon. Not. R. Astron. Soc.* **469**, 435–447 (2017).
- 5 T. H. Vidal and V. Wakelam, “A new look at sulphur chemistry in hot cores and corinos,” *Mon. Not. R. Astron. Soc.* **474**, 5575–5587 (2018).
- 6 J. C. Laas and P. Caselli, “Modeling sulfur depletion in interstellar clouds,” *Astron. Astrophys.* **624**, A108 (2019).
- 7 D. E. Woon, see http://www.astronomer.org/astronomist_ism.html for Interstellar and circumstellar molecules; accessed August 08, 2023.
- 8 A. Maris, C. Calabrese, L. B. Favero, L. Evangelisti, I. Usabiaga, S. Mariotti, C. Codella, L. Podio, N. Balucani, C. Ceccarelli, B. LeFloch, and S. Melandri, “Laboratory measurements and astronomical search for thioacetamide,” *ACS Earth Space Chem.* **3**, 1537–1549 (2019).
- 9 A. Remijan, C. Xue, L. Margulès, A. Belloche, R. A. Motiyenko, J. Carder, C. Codella, N. Balucani, C. L. Brogan, C. Ceccarelli, T. R. Hunter, A. Maris, S. Melandri, M. Siebert, and B. A. McGuire, “Expanding the submillimeter wave spectroscopy and astronomical search for thioacetamide (CH₃CSNH₂) in the ISM,” *Astron. Astrophys.* **658**, A85 (2022).
- 10 U. Anthoni, P. H. Nielsen, and D. H. Christensen, “Assignment of the infrared spectrum of thioacetamide single crystals from low-temperature polarization measurements combined with ¹³C and ¹⁵N isotopic shifts,” *Spectrochim. Acta, Part A* **41**, 1327–1334 (1985).
- 11 S. Sankar Bala, P. K. Panja, P. N. Ghosh, S. Sankar Bala, P. K. Panja, P. N. Ghosh, S. S. Bala, P. K. Panja, and P. N. Ghosh, “Vibrational spectra of acetamide and thioacetamide at low temperature: Fermi resonance and hydrogen bond studies,” *J. Mol. Struct.* **157**, 339–351 (1987).
- 12 S. Góbi, I. Reva, G. Tarczay, and R. Fausto, “Amorphous and crystalline thioacetamide ice: Infrared spectra as a probe for temperature and structure,” *J. Mol. Struct.* **1220**, 128719 (2020).
- 13 L. Lapinski, H. Rostkowska, A. Khvorostov, and M. J. Nowak, “UV induced proton transfer in thioacetamide: First observation of thiol form of simple thioamide,” *Phys. Chem. Chem. Phys.* **5**, 1524–1529 (2003).
- 14 X. Chen, Y. Zhao, H. Zhang, J. Xue, and X. Zheng, “Excited state proton transfer dynamics of thioacetamide in S₂($\pi\pi^*$) state: Resonance Raman spectroscopic and quantum mechanical calculations study,” *J. Phys. Chem. A* **119**, 832–842 (2015).
- 15 S. Góbi, C. M. Nunes, I. Reva, G. Tarczay, and R. Fausto, “S–H rotamerization via tunneling in a thiol form of thioacetamide,” *Phys. Chem. Chem. Phys.* **21**, 17063–17071 (2019).
- 16 S. Góbi, I. Reva, I. P. Csonka, C. M. Nunes, G. Tarczay, and R. Fausto, “Selective conformational control by excitation of NH imino vibrational antennas,” *Phys. Chem. Chem. Phys.* **21**, 24935–24949 (2019).
- 17 M. J. Abplanalp, A. Borsuk, B. M. Jones, and R. I. Kaiser, “On the formation and isomer specific detection of propenal (C₂H₃CHO) and cyclopropanone (c-C₃H₄O) in interstellar model ices—A combined FTIR and reflectron time-of-flight mass spectroscopic study,” *Astrophys. J.* **814**, 45 (2015).
- 18 M. Tsuge and Y.-P. Lee, “Spectroscopy of molecules confined in solid *para*-hydrogen,” in *Molecular and Laser Spectroscopy*, edited by V. Gupta and Y. Ozaki (Elsevier, Amsterdam, 2020), Chap. V, pp. 167–215.
- 19 J. R. Sodeau and E. K. C. Lee, “Photooxidation of sulfur dioxide in low-temperature matrices,” *J. Phys. Chem.* **84**, 3358–3362 (1980).
- 20 L. S. Chen, C. I. Lee, and Y. P. Lee, “Isomers of SO₂: Infrared absorption of SOO in solid argon,” *J. Chem. Phys.* **105**, 9454–9460 (1996).
- 21 S. Góbi, I. P. Csonka, G. Bazsó, and G. Tarczay, “Successive hydrogenation of SO and SO₂ in solid *para*-H₂: Formation of elusive small oxoacids of sulfur,” *ACS Earth Space Chem.* **5**, 1180–1195 (2021).
- 22 S. H. Jou, M. Y. Shen, C. H. Yu, and Y. P. Lee, “Isomers of SO₃: Infrared absorption of OSOO in solid argon,” *J. Chem. Phys.* **104**, 5745–5753 (1996).
- 23 E. Isoniemi, M. Pettersson, L. Khriachtchev, J. Lundell, and M. Räsänen, “Infrared spectroscopy of H₂S and SH in rare-gas matrixes,” *J. Phys. Chem. A* **103**, 679–685 (1999).
- 24 E. Isoniemi, L. Khriachtchev, M. Pettersson, and M. Räsänen, “Infrared spectroscopy and 266 nm photolysis of H₂S₂ in solid Ar,” *Chem. Phys. Lett.* **311**, 47–54 (1999).
- 25 E. Isoniemi, L. Khriachtchev, J. Lundell, and M. Räsänen, “HSO₂ isomers in rare-gas solids,” *Phys. Chem. Chem. Phys.* **4**, 1549–1554 (2002).

- ²⁶J. Fournier, C. Lalo, J. Deson, and C. Vermeil, "Thermoluminescence following VUV photolysis of OCS and CS₂ in an argon matrix," *J. Chem. Phys.* **66**, 2656–2659 (1977).
- ²⁷M. E. Jacox and D. E. Milligan, "Matrix isolation study of the infrared spectrum of thioformaldehyde," *J. Mol. Spectrosc.* **58**, 142–157 (1975).
- ²⁸J. Purzycka, T. Custer, and M. Gronowski, "UV photolysis of C₂H₅SH in solid CO and Ar," *ACS Earth Space Chem.* **6**, 131–143 (2022).
- ²⁹J. Zapala, T. Custer, J. C. Guillemin, and M. Gronowski, "Photochemistry of XCH₂CN (X = -Cl, -SH) in argon matrices," *J. Phys. Chem. A* **123**, 3818–3830 (2019).
- ³⁰N. F. W. Ligterink, D. M. Paardekooper, K. J. Chuang, M. L. Both, G. A. Cruz-Diaz, J. H. van Helden, and H. Linnartz, "Controlling the emission profile of an H₂ discharge lamp to simulate interstellar radiation fields," *Astron. Astrophys.* **584**, A56 (2015).
- ³¹S. Góbi, M. J. Abplanalp, and R. I. Kaiser, "Effect of perchlorates on electron radiolysis of Glycine with application to Mars," *Astrophys. J.* **822**, 8 (2016).
- ³²G. Bazsó, I. P. Csonka, S. Góbi, and G. Tarczay, "VIZSLA—Versatile ice zigzag sublimation setup for laboratory astrochemistry," *Rev. Sci. Instrum.* **92**, 124104 (2021).
- ³³M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, GAUSSIAN 09 Revision D.01, Gaussian, Inc., 2013.
- ³⁴M. Wierzejewska and R. Wieczorek, "Infrared matrix isolation and ab initio studies on isothiocyanic acid HNCS and its complexes with nitrogen and xenon," *Chem. Phys.* **287**, 169–181 (2003).
- ³⁵M. Wierzejewska and Z. Mielke, "Photolysis of isothiocyanic acid HNCS in low-temperature matrices. Infrared detection of HSCN and HSNC isomers," *Chem. Phys. Lett.* **349**, 227–234 (2001).
- ³⁶S. V. Kameneva, A. D. Volosatova, and V. I. Feldman, "Radiation-induced transformations of isolated CH₃CN molecules in noble gas matrices," *Radiat. Phys. Chem.* **141**, 363–368 (2017).
- ³⁷A. Givan, A. Loewenschuss, K. Bier, and H. Jodl, "The fundamental vibrations of CS₂ as probes of matrix effects in matrix isolation spectroscopy," *Chem. Phys.* **106**, 151–159 (1986).
- ³⁸F. H. Frayer and G. E. Ewing, "Nuclear-spin conversion and vibration-rotation spectra of methane in solid argon," *J. Chem. Phys.* **48**, 781 (1968).
- ³⁹M. Ruzi and D. T. Anderson, "Photodissociation of N-methylformamide isolated in solid parahydrogen," *J. Chem. Phys.* **137**, 194313 (2012).
- ⁴⁰J. R. Durig and D. W. Wertz, "On the infrared spectra of HNCS and DNCS," *J. Chem. Phys.* **46**, 3069–3077 (1967).
- ⁴¹Y. F. Lee and Y. P. Lee, "Infrared absorption of CH₃SO₂ observed upon irradiation of a p-H₂ matrix containing CH₃I and SO₂," *J. Chem. Phys.* **134**, 124314 (2011).
- ⁴²T. Momose, M. Miki, T. Wakabayashi, T. Shida, M. C. Chan, S. S. Lee, and T. Oka, "Infrared spectroscopic study of rovibrational states of methane trapped in parahydrogen crystal," *J. Chem. Phys.* **107**, 7707–7716 (1997).
- ⁴³T. Shimanouchi, *Tables of Molecular Vibrational Frequencies Consolidated Volume I* (National Bureau of Standards, 1972), p. 160.
- ⁴⁴F. Ito, T. Nakanaga, K. i. Sugawara, H. Takeo, M. Sugie, C. Matsumura, and Y. Hamada, "Observation of the high-resolution infrared spectrum of the ν₄ band of ketenimine, CH₂CNH," *J. Mol. Spectrosc.* **140**, 177–184 (1990).
- ⁴⁵H. W. Kroto and D. McNaughton, "Fourier transform infrared spectrum of thioketene, CH₂CS," *J. Mol. Spectrosc.* **114**, 473–482 (1985).
- ⁴⁶M. Ruzi and D. T. Anderson, "Matrix isolation spectroscopy and nuclear spin conversion of NH₃ and ND₃ in solid parahydrogen," *J. Phys. Chem. A* **117**, 9712–9724 (2013).
- ⁴⁷C. J. Bennett, C. Jamieson, A. M. Mebel, and R. I. Kaiser, "Untangling the formation of the cyclic carbon trioxide isomer in low temperature carbon dioxide ices," *Phys. Chem. Chem. Phys.* **6**, 735–746 (2004).
- ⁴⁸J. Krupa, I. Kosendiak, and M. Wierzejewska, "New data on photochemistry of the interstellar molecule: HNCS. Identification of the S · · HCN complex," *Phys. Chem. Chem. Phys.* **17**, 22431–22437 (2015).
- ⁴⁹D. E. Milligan and M. E. Jacox, "Spectroscopic study of the vacuum-ultraviolet photolysis of matrix-isolated HCN and halogen cyanides. Infrared spectra of the species CN and XNC," *J. Chem. Phys.* **47**, 278–285 (1967).
- ⁵⁰G. Maier, C. Schmidt, H. P. Reisenauer, E. Endlein, D. Becker, J. Eckwert, B. H. Andes Jr, and L. J. Schaad, "Blausäure-N-methylid: Darstellung, spektroskopische eigenschaften und seine beziehung zu anderen C₂H₂N-isomeren," *Chem. Ber.* **126**, 2337–2352 (1993).
- ⁵¹M. A. Frerking, R. A. Linke, and P. Thaddeus, "Interstellar isothiocyanic acid," *Astrophys. J.* **234**, L143 (1979).
- ⁵²H. Feuchtgruber, F. P. Helmich, E. F. van Dishoeck, and C. M. Wright, "Detection of interstellar CH₃," *Astrophys. J.* **535**, L111–L114 (2000).
- ⁵³J. H. Lacy, J. S. Carr, N. J. I. Evans, F. Baas, J. M. Achtermann, and J. F. Arens, "Discovery of interstellar methane: Observations of gaseous and solid CH₄ absorption toward young stars in molecular clouds," *Astrophys. J.* **376**, 556–560 (1991).
- ⁵⁴P. M. Solomon, K. B. Jefferts, A. A. Penzias, and R. W. Wilson, "Detection of millimeter emission lines from interstellar methyl cyanide," *Astrophys. J.* **168**, L107 (1971).
- ⁵⁵D. A. Neufeld, E. Falgarone, M. Gerin, B. Godard, E. Herbst, G. Pineau Des Forêts, A. I. Vasyunin, R. Güsten, H. Wiesemeyer, and O. Ricken, "Discovery of interstellar mercapto radicals (SH) with the GREAT instrument on SOFIA," *Astron. Astrophys.* **542**, L6 (2012).
- ⁵⁶P. Thaddeus, M. L. Kutner, A. A. Penzias, R. W. Wilson, and K. B. Jefferts, "Interstellar hydrogen sulfide," *Astrophys. J.* **176**, L73–L76 (1972).
- ⁵⁷J. Cernicharo, C. Cabezas, M. Agúndez, B. Tercero, J. R. Pardo, N. Marcelino, J. D. Gallego, F. Tercero, J. A. López-Pérez, and P. De Vicente, "TMC-1, the starless core sulfur factory: Discovery of NCS, HCCS, H₂CCS, H₂CCCS, and C₄S and detection of C₅S," *Astron. Astrophys.* **648**, L3 (2021).
- ⁵⁸A. C. Cheung, D. M. Rank, C. H. Townes, D. D. Thornton, and W. J. Welch, "Detection of NH₃ molecules in the interstellar medium by their microwave emission," *Phys. Rev. Lett.* **21**, 1701–1705 (1968).
- ⁵⁹L. E. Snyder and D. Buhl, "Observations of radio emission from interstellar hydrogen cyanide," *Astrophys. J.* **163**, L47–L52 (1971).
- ⁶⁰L. E. Snyder and D. Buhl, "Detection of several new interstellar molecules," *Ann. N. Y. Acad. Sci.* **194**, 17–24 (1972).
- ⁶¹B. Zuckerman, M. Morris, P. Palmer, and B. E. Turner, "Observations of CS, HCN, U89.2, and U90.7 in NGC 2264," *Astrophys. J.* **173**, L125–L129 (1972).
- ⁶²G. L. Blackman, R. D. Brown, P. D. Godfrey, and H. I. Gunn, "The microwave spectrum of HNC: Identification of U90.7," *Nature* **261**, 395–396 (1976).
- ⁶³S. Nickerson, N. Rangwala, S. W. J. Colgan, C. DeWitt, X. Huang, K. Acharyya, M. Drozdovskaya, R. C. Fortenberry, E. Herbst, and T. J. Lee, "The first mid-infrared detection of HNC in the interstellar medium: Probing the extreme environment toward the orion hot core," *Astrophys. J.* **907**, 51 (2021).