

Astrochemically relevant H-atom-abstraction and H-atom-addition reactions connecting fulminic acid (HCNO) and formaldoxime (H₂CNOH)

Barbara Keresztes,^{1,2} Sándor Góbi,³ István Pál Csonka,³ Gopi Ragupathy,³ Gábor Bazsó⁴ and György Tarczay^{1,3,5★}

¹Laboratory of Molecular Spectroscopy, Institute of Chemistry, ELTE Eötvös Loránd University, PO Box 32, H-1518 Budapest, Hungary

²Hevesy György PhD School of Chemistry, Institute of Chemistry, ELTE Eötvös Loránd University, PO Box 32, H-1518 Budapest, Hungary

³MTA-ELTE Lendület Laboratory Astrochemistry Research Group, Institute of Chemistry, ELTE Eötvös Loránd University, PO Box 32, H-1518 Budapest, Hungary

⁴Wigner Research Centre for Physics, PO Box 49, H-1525 Budapest, Hungary

⁵Centre for Astrophysics and Space Science, ELTE Eötvös Loránd University, PO Box 32, H-1518 Budapest, Hungary

Accepted 2023 February 27. in original form 2023 February 3

ABSTRACT

While fulminic acid (HCNO) is a well-known interstellar molecule, its partially hydrogenated form, formaldoxime (H₂CNOH), has not been detected yet in the interstellar medium (ISM). A possible reason for the non-detection of H₂CNOH can be that in the presence of H atoms the quasi-equilibrium between these species is shifted towards HCNO. To support this hypothesis, the H-atom-abstraction and H-atom-addition reactions of HCNO and H₂CNOH were investigated in solid *para*-H₂ matrix at 3.1 K. The reactions were followed by IR spectroscopy. The experiments proved that both the H-atom-addition reaction to HCNO and the H-atom-abstraction reaction from H₂CNOH proceed at low temperatures, and these reactions yield H₂CNO radical. In addition, H-atom-addition reaction can also take place with H₂CNOH, leading to the formation of H₃CNOH radical. Both H₂CNO and H₃CNOH radicals can react with H atoms, either in a H-atom-addition reaction or in a H-atom-abstraction reaction. Although all of these reactions are barrierless, experimentally the H-atom-addition reactions were not observed, revealing that the H-atom-abstraction reactions of these radicals are more effective. Therefore, in the case of a quasi-equilibrium condition, the abundance of H₂CNOH in the ISM is expected to be lower than that of HCNO. Furthermore, the results also indicate that the H-atom-addition and H-atom-abstraction reactions between H₂CNOH and HCNO can act as catalytic cycles for interstellar H₂ formation.

Key words: astrochemistry – molecular processes – methods: laboratory: molecular – ISM: molecules.

1 INTRODUCTION

The [H, C, N, O] isomers are thoroughly examined molecules of the interstellar medium (ISM). The thermodynamically most stable isomer, isocyanic acid (HNCO), was identified in the ISM, namely in Sgr B2, as early as 1972 (Snyder & Buhl 1972). The second isomer, cyanic acid (HOCN), was found in Sgr B2 in 2009 (Brünken et al. 2009, 2010). Observations towards different regions of Sgr B2 and towards several other sources showed that the HNCO/HOCN ratio is varying in the range of 30 to 300 (Brünken et al. 2010; Marcelino et al. 2010). The third isomer in energy, fulminic acid (HCNO), was observed first also in 2009, in dark molecular clouds: in starless cores, B1, L1544, and L183, and in the low-mass star-forming region L1527 (Marcelino et al. 2009). The HNCO/HCNO ratio in these objects was measured between 40 and 70. The fourth, the highest energy singlet isomer, isofulminic acid (HONC), was characterized in the laboratory by microwave spectroscopy (Mladenović et al. 2009), but its interstellar detection has not yet been reported. Different models were considered to explain the relative abundances of these four

isomers in the gaseous ISM, including gas-phase and/or grain surface formation and destruction routes (Marcelino et al. 2010; Quan et al. 2010) and different sublimation temperatures and possible partial isomerization upon sublimation (Lattalais et al. 2009, 2015).

A partially hydrogenated form of HNCO, formamide (H₂NC(H)O), is a well-known important interstellar molecule that was observed even earlier than HNCO, also in Sgr B2 (Rubin et al. 1971, 1972). Later, astronomical observations revealed that almost a constant ratio exists between HNCO and H₂NC(H)O in pre- and protostellar environments over six orders of magnitude in luminosity (López-Sepulcre et al. 2015). On the basis of this result and other reports, it was proposed that interstellar H₂NC(H)O is likely formed by the hydrogenation of HNCO on icy grains. Contrary to this hypothesis, Noble et al. (2015) were able to prove only H/D exchange when HNCO ice was bombarded by D atoms, but no H₂NC(H)O formation was observed in a detectable amount upon bombarding H atoms on to HNCO ice near 10 K (Noble et al. 2015). Shortly after these experiments, Haupa, Tarczay & Lee (2019a) investigated the reactions of H atoms with H₂NC(H)O in solid *para*-H₂. It was shown that H₂NC(H)O, H₂NCO radical, and HNCO are indeed connected by a dual-cycle reaction mechanism, consisting of H-atom-addition and H-atom-abstraction reactions, and the quasi-

★ E-mail: gyorgy.tarczay@ttk.elte.hu

equilibrium is shifted towards the dehydrogenated HNCO product. Therefore, the existence of mechanism can be a plausible explanation for the constant ratio of $\text{H}_2\text{NC(H)O}$ and HNCO in the ISM. The other important conclusion of this study was that since H_2 is formed in this dual-cycle mechanism, HNCO and $\text{H}_2\text{NC(H)O}$ might contribute to the catalytic formation of interstellar H_2 on icy grain surfaces. Suhasaria & Mennella (2020) have also proved that the reaction of H atoms with solid $\text{H}_2\text{NC(H)O}$ at 12 K also leads to the formation of HNCO. By mapping the $\text{H}_2\text{NC(H)O}$ and HNCO abundances in HH 112 protostellar disc, Lee et al. (2022) found the same spatial distribution, kinematics, and temperature for these two species. By considering that HNCO has much lower binding energy to grain surfaces than $\text{H}_2\text{NC(H)O}$, they arrived at the conclusion that HNCO is likely a daughter species of desorbed $\text{H}_2\text{NC(H)O}$.

A partially hydrogenated form of HCNO is formaldoxime (H_2CNOH). Formaldoxime was thoroughly studied by spectroscopic methods, including gas-phase micro- and millimeterwave spectroscopy (Levine 1962, 1963; Pillai 1962; Kaushik & Takagi 1978; Klesing & Sutter 1990; Zou et al. 2021), high-resolution IR (Duxbury 1988; Duxbury et al. 1988; Bannai & Duxbury 1994; Wu & Tan 2020; Tan, Jusuf & Wu 2021; Wu & Tan 2021; Jusuf, Tan & Wu 2022), and matrix-isolation IR spectroscopy (Heikkilä et al. 1999; Golec & Mielke 2007; Golec, Grzegorzec & Mielke 2008; Golec, Bil & Mielke 2009; Golec et al. 2015). As a potential interstellar molecule, formaldoxime was searched in the ISM since the 1970s, but it could not be detected yet. A possible explanation for the non-detection of formaldoxime might be the existence of a similar dual-cycle mechanism that was described for HNCO and $\text{H}_2\text{NC(H)O}$. If HCNO and formaldoxime are also connected in this way and the quasi-equilibrium is also shifted to the dehydrogenated form, then considering the observed HCNO/HNCO ratio in the ISM, formaldoxime should have a very low abundance in the ISM. The aim of this study is to verify this hypothesis.

Here, we took the advantage of the *para*- H_2 matrix-isolation method to study the astrophysically relevant low-temperature reactions of formaldoxime and HCNO with H atoms. Besides the above-mentioned $\text{H}_2\text{NC(H)O}$ experiment (Haupa et al. 2019a), this method was already used for the investigation of H-atom-addition and H-atom-abstraction reactions of many other molecules of astrochemical interest, including e.g. HONO (Haupa, Tielens & Lee 2017), SO and SO_2 (Góbi et al. 2021), methyl formate (HC(O)OCH_3) (Haupa et al. 2019b), acetamide (CH_3CONH_2) (Haupa, Ong & Lee 2020), glycine ($\text{H}_2\text{NCH}_2\text{COOH}$) (Schneiker et al. 2021), *N*-methylformamide ($\text{HC(O)NH(CH}_3\text{)}$) (Tsai, Haupa & Lee 2022), methylamine (CH_3NH_2) (Joshi & Lee 2022), and furan (cyclo- $\text{C}_4\text{H}_4\text{O}$) (Schneiker et al. 2022). The advantages of studying interstellar H atom reactions by this method are discussed in recent review and conference papers (Tsuge, Tseng & Lee 2018; Tarczay, Haupa & Lee 2019; Haupa, Joshi & Lee 2022).

Although the *para*- H_2 matrix environment is apolar and colder (<4 K) than the typical interstellar ice environments, it is a preferred method to study astrophysically relevant H atom reactions as a first step. In this quantum host, the interaction between the isolated molecules and the *para*- H_2 is negligible, therefore the spectra of molecules frozen into this matrix consist of sharp bands, and it can be compared very well with gas-phase spectral data or quantum chemical computations. This offers unambiguous spectral assignments in most of the cases. Furthermore, H atoms can effectively be generated in *para*- H_2 e.g. by a two-step photolysis of Cl_2 frozen into the host. (See details in the next section.) While the diffusion of the Cl_2 , Cl atoms, HCl (obtained as a by-product of the photolysis), and the isolated investigated molecules is mostly blocked below

4 K, the H atom can move efficiently in the *para*- H_2 by quantum diffusion (Fushitani & Momose 2003; Ruzi & Anderson 2015; Balabanoff, Ruzi & Anderson 2018). These facts make this method more sensitive for studying low-temperature H atom reactions of astrochemical species as compared to the conventional method when the pure ice of the investigated molecule or astrophysical analogue ices containing the investigated molecule is bombarded by H atoms. If a reaction proceeds in solid *para*- H_2 , the reaction is very likely feasible also under astrophysical conditions, in a polar environment and at a somewhat higher temperature. Therefore, the *para*- H_2 matrix-isolation method can be used to sensitively pre-screen the H atom reactions, then, these reactions can be verified by less sensitive experiments performed on the surface or in the bulk astrophysical ices.

2 MATERIALS AND METHODS

The experiments were carried out in the ultrahigh-vacuum compatible stainless steel chamber of the VIZSLA set-up (Bazsó et al. 2021). The chamber can be evacuated to a base pressure of 1×10^{-8} mbar. Inside the chamber, there is a gold-coated silver substrate whereupon the deposition of the matrix occurs during the experiments. The substrate is mounted on the cold finger of an RDK-415D2 cryostat (Sumitomo Heavy Industries Inc.), which allows the substrate to be cooled down to $T = 3.1$ K.

The *para*- H_2 was generated by flowing *normal*- H_2 through Fe_2O_3 catalyst (SigmaAldrich, hydrated, catalyst grade, 30–50 mesh) at $T = 13.9$ K. After that, the prepared *para*- H_2 was collected in a 1 L glass bulb on a vacuum line connected to the VIZSLA set-up. This *para*- H_2 was used to prepare the matrix thereafter.

Formaldoxime was generated by the thermal decomposition of formaldoxime trimer hydrogen chloride complex (Aldrich, 98 per cent), while HCNO, together with other [H, C, N, O] isomers, were prepared after matrix deposition, by *in situ* photolysis of 1,2,5-oxadiazole. 1,2,5-oxadiazole was prepared for a previous experiment (Keresztes et al. 2020). Before the experiments, these precursors were placed in sample holders; the 1,2,5-oxadiazole was placed into a glass vial connected to the premixing vacuum line, while formaldoxime was inserted into a glass sample holder tube inside a stainless steel oven located in front of the substrate, inside the ultra-high-vacuum chamber of the VIZSLA set-up.

In the case of 1,2,5-oxadiazole, the sample was mixed with the previously collected *para*- H_2 in a 0.5 L bulb on the vacuum line (the mixing was done in two steps, homogenization times of approximately 45 and 30 min were applied after each step, respectively; the final precursor : *para*- H_2 ratio was approximately 1 : 2300). Then, this mixture was co-deposited with Cl_2 on the substrate through a stainless steel capillary array ending approximately 3 cm away from the substrate. In the case of formaldoxime, the precursor was sublimated at $T = 39.5$ °C (the temperature was measured by a K-type thermocouple and controlled by a Lakeshore Model 336 controller) and was co-frozen with *para*- H_2 and Cl_2 on the substrate. Upon these conditions, the precursor decomposes to formaldoxime monomer and hydrogen chloride. These were mixed with *para*- H_2 and Cl_2 immediately before the deposition.

The inlet rates of the pure *para*- H_2 or the 1,2,5-oxadiazole : *para*- H_2 mixture and Cl_2 were regulated by two separate leak valves. In the matrix, the Cl_2 : *para*- H_2 ratio was approximately 1 : 500–1 : 1000 in both experiments. For blank experiments Cl_2 was not deposited. The sample deposition was monitored by means of Fourier-transform infrared spectroscopy (FTIR) mid-IR (MIR) spectrometer in reflection-absorption mode. The IR spectra were

recorded by a Bruker Invenio FTIR spectrometer in the 4000–600 cm^{−1} spectral range at a resolution of 0.5 cm^{−1}, averaging 32–128 scans for each spectrum using a liquid-N₂-cooled mid-band mercury cadmium telluride detector.

After the matrix deposition the purity of *para*-H₂ was checked by recording the NIR spectrum of the deposited matrix and measuring the relative absorption of the band belonging to *ortho*-H₂ (Q₁(0) + S₀(1) transition) at 4740 cm^{−1}. The NIR spectra were recorded in the range 9000–600 cm^{−1} at a resolution of 0.5 cm^{−1}.

In the first set of experiments, formaldoxime was irradiated with laser UV light at a wavelength of 365 nm (for 60–90 min) to photolyse the Cl₂ molecules and produce Cl atoms. Due to the diminished cage effect in *para*-H₂, the two Cl atoms are separated and they do not recombine. The Cl atoms do not react with *para*-H₂ molecules but the reaction can be initiated after the excitation of the Q₁(1) + S₀(0) and Q₁(0) + S₀(0) combination band of *para*-H₂. The excitation was carried out by IR light irradiation at a wavelength of 2217 nm (70–110 min). After the H atom generation, the sample was kept in dark overnight. During this period H atoms can diffuse in the matrix and they can react with the sample.

In the second set of experiments, the 1,2,5-oxadiazole was irradiated for roughly 3.5 h with laser UV light at 220 nm in order to photolyse the precursor and form the [H, C, N, O] isomers. This photolysis resulted in over 80 percent decomposition of the 1,2,5-oxadiazole precursor. Then, as in the case of the first set of experiments, the matrix was irradiated by 365 and 2217 nm laser light, to produce Cl and then H atoms and HCl, respectively. Then the sample was kept in the dark through the night.

In both cases, the chemical changes were followed by recording the MIR spectra of the matrix after each step and regularly during the night process. Both of the experiments were then completed by secondary photolysis studies. This is supposed to help with the identification of hydrogenation products, as the different products may decompose at different rates at different wavelengths; therefore, the bands in the IR spectra can be grouped based on the qualitative behaviour of the species upon irradiation. Upon the secondary photolysis, the sample was irradiated sequentially with UV laser light at different wavelengths between 365 and 220 nm for approximately 30 min, and MIR spectra were collected after each step.

All laser irradiations were carried out by an optical parametric oscillator (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* ≈ 2.1–2.2 W, *λ* = 355 nm, *f* = 10 Hz, pulse duration = 2–3 ns). The chemical changes during the photodecomposition were followed by recording the MIR spectra of the sample. During the 365 nm irradiation, NIR spectra were recorded to monitor the formation of Cl atoms (5095 cm^{−1}). The H atom generation was followed by monitoring the MIR absorption band of HCl at 2894 cm^{−1}.

In the case of both 1,2,5-oxadiazole and formaldoxime, blank experiments with a sample containing no chlorine were also carried out to ensure that the 365 nm UV laser light used to produce Cl atoms does not result in the decomposition of formaldoxime and [H, C, N, O] isomers. In the case of the 1,2,5-oxadiazole experiment, the 365 nm irradiation was preceded by 220 nm irradiation, as the same was done in the actual H-atom-reaction experiment. The experiments were repeated with a matrix containing 1,2,5-oxadiazole and chlorine but without 220 nm irradiation, i.e. without photodecomposition of the 1,2,5-oxadiazole precursor, to identify the bands of the possible reaction products of H atoms and 1,2,5-oxadiazole.

Mixing ratios were estimated using the method described by Tsuge & Lee (2020). The integrated areas of the absorption bands

with the highest intensities for each species were normalized with the corresponding computed anharmonic IR intensity of the particular vibrational band and then these were averaged. The upper limit of the H atom mixing ratio can be estimated from the intensity of the HCl absorption line at 2894.1 cm^{−1} and from the thickness of the matrix. The optical path length (and therefore the thickness) can be determined from the integrated *para*-H₂ band areas in the 4520–4495 cm^{−1} (Q₁(0) + S₀(0) transition) and 4855–4825 cm^{−1} (S₁(0) + S₀(0) transition) regions using the IR absorption coefficients of 90 ± 2 and 7.0 ± 0.2 cm^{−2}, respectively. By taking into consideration the angle of incidence of the beam of the IR beam (60° to the surface normal of the substrate), we estimate the thickness of the matrix to be 0.126 ± 0.003 (formaldoxime experiment) and 0.101 ± 0.003 mm (1,2,5-oxadiazole experiment), respectively.

To predict the reaction paths and to help the identification of reaction products, quantum chemical computations were carried out with the help of the GAUSSIAN 09 (Frisch et al. 2009) and CFOUR (Matthews et al. 2020; Stanton et al. 2020) program packages. First, the minimum-energy structures and the transition states (TSs) were located on the potential energy surface (PES) at the B3LYP/cc-pVTZ level of theory. Then, harmonic and anharmonic vibrational frequencies together with IR intensities were computed at the same level of theory. To get better estimates for vibrational frequencies, geometry optimizations were also performed at the frozen-core CCSD(T)/cc-pVTZ level of theory, followed by harmonic vibrational frequency computations. The best estimate for the vibrational frequency of each normal mode was obtained as the sum of CCSD(T)/cc-pVTZ harmonic vibrational frequency and B3LYP/cc-pVTZ anharmonic correction.

3 RESULTS AND DISCUSSION

3.1 Computational results

Fig. 1 shows the structure and the zero-point vibrational energy (ZPVE) corrected relative energy of all hydrogenated and dehydrogenated species of [H, C, N, O] isomers and the two forms of formaldoxime at the B3LYP/cc-pVTZ level of theory. The anharmonic vibrational frequencies with their intensities were computed for all hydrogenated and dehydrogenated species of [H, C, N, O] isomers and formaldoxime as well; they are listed in the Supporting Information. Besides fulminic acid (HCNO), other [H, C, N, O] isomers have to be also considered because they are formed in our experiments, from the 1,2,5-oxadiazole precursor upon the 220 nm photolysis. In addition, Fig. 1 also shows the low-energy hydrogenated structures of those [2H, C, N, O], [3H, C, N, O], [4H, C, N, O], and [5H, C, N, O] isomers that might be produced upon the reaction of H atoms and formaldoxime. Note that in former studies the two isomers of formaldoxime were labelled as *trans* and *cis* (Heikkilä et al. 1999; Zou et al. 2021). In this study, to avoid confusion with the *trans* and *cis* notation of the ligands around the CN bond in other species, the *anti* and *syn* nomenclature is used for the CNOH torsion. The computed geometries and vibrational frequencies and intensities of the structures shown in Fig. 1 and those of the TS structures are given in Tables S1–S33 of the Supporting Information.

Fig. 2 visualizes the PES of the H-atom-addition, whereas Fig. 3 displays the PES of the H-atom-abstraction reactions. The figures include only the *anti*-H₂CNOH because the *syn* form is not present when formaldoxime is deposited in an inert apolar matrix (Heikkilä et al. 1999). The relative energies of the species corresponding to the sequential reaction steps and those of the TSs without and with

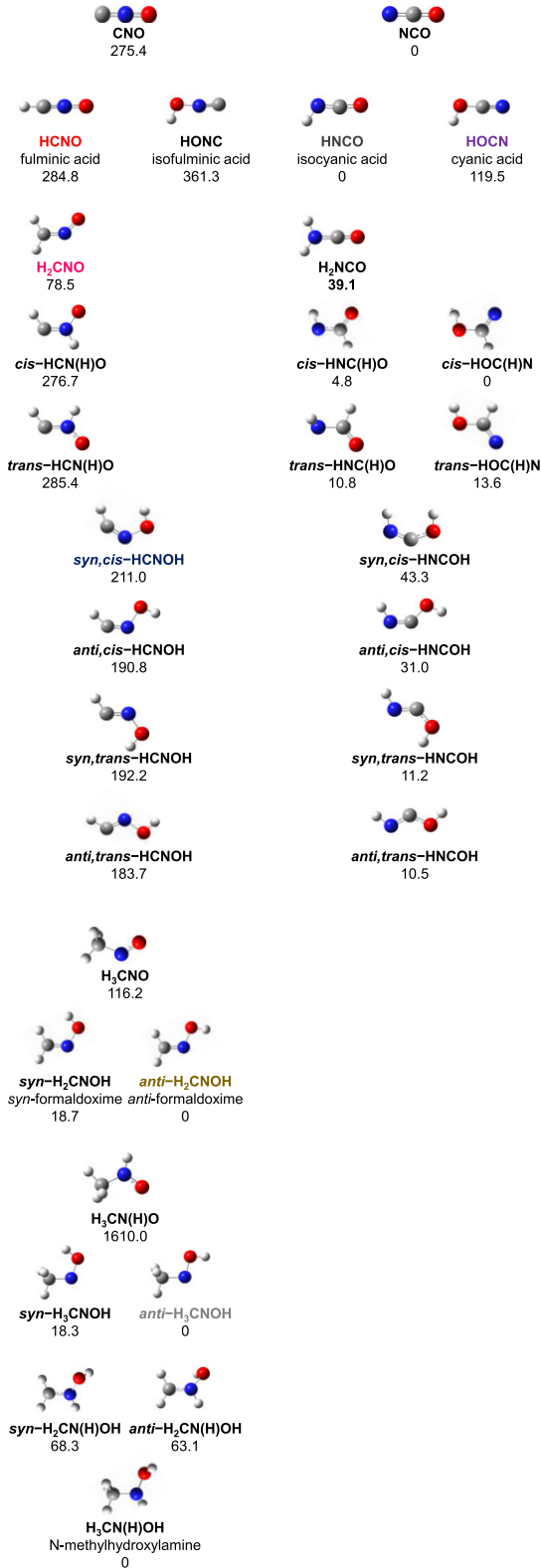


Figure 1. Structures and ZPVE-corrected relative energies (in kJ mol^{-1}) of low-energy $[n\text{H}, \text{C}, \text{N}, \text{O}]$ $n=0-5$ isomers as obtained at the B3LYP/cc-pVTZ level of theory. For reference energy, the energy of the thermodynamically most stable isomer was considered for each n . For $n=4$ and 5 only the structures that can be formed in an H-atom-addition reaction of formaldoxime are shown. (The colours of the coloured formulas will be used as visual aids in spectrum assignments.).

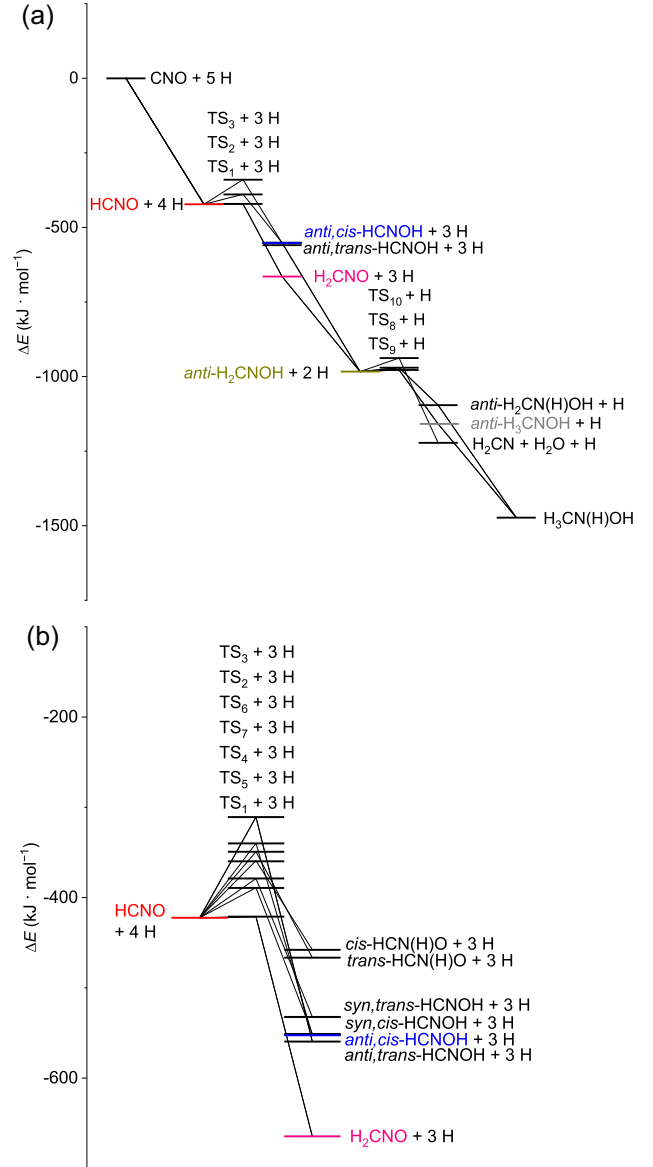


Figure 2. PES of H-atom-addition reactions of HCNO as computed at the B3LYP/cc-pVTZ level of theory. (a) PES from $\text{CNO} + 5\text{H}$ to $\text{H}_3\text{CN}(\text{H})\text{OH}$ via HCNO and $\text{anti-H}_2\text{CNOH}$. (b) A detailed PES that shows all the possible singlet $[2\text{H}, \text{C}, \text{N}, \text{O}]$ species that can be formed in the reaction of HCNO with H atoms. All energies include ZPVE correction.

ZPVE correction, by taking $\text{CNO} + 5\text{H}$ and $\text{H}_3\text{CN}(\text{H})\text{OH} + 5\text{H}$ as the reference, for H-atom-addition and H-atom-abstraction reaction, respectively, are listed in Table 1.

Starting from CNO radical, the first H-atom-addition, resulting HCNO, is a radical–radical recombination process; therefore, it is barrierless. The addition of the second H atom can result in different isomers. The addition of the second H atom to the O atom of HCNO can lead to the formation of four different structures. Among these syn,cis-HCNOH can be formed via the lowest energy barrier from HCNO. This barrier is computed to be 33.4 kJ mol^{-1} at the B3LYP/cc-pVTZ level of theory with ZPVE correction (Table 1 and Fig. 2). Taking into consideration the computational uncertainty, this reaction might proceed very slowly by H-atom tunnelling at a few K. The barriers leading to the other three isomers are between 43.6 and $111.7 \text{ kJ mol}^{-1}$, and the H-atom tunnelling reactions with this

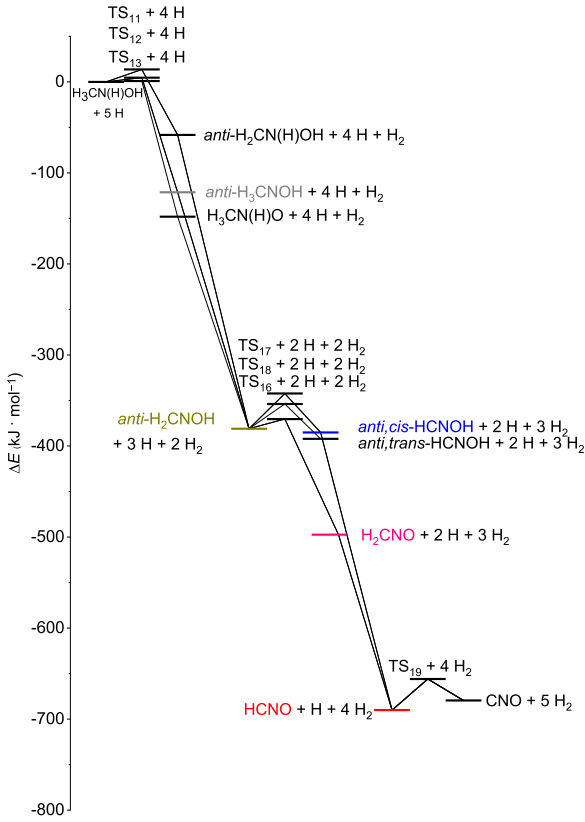


Figure 3. PES of H-atom-abstraction reactions via *anti*-H₂CNOH and HCNO as computed at the B3LYP/cc-pVTZ level of theory. All energies include ZPVE correction.

barrier height are not expected to proceed on the laboratory time-scale. Nevertheless, the isomerization barrier from *syn,cis*-HCNOH to the thermodynamically more favoured *anti,cis*-HCNOH is only 13.1 kJ mol⁻¹ therefore this isomerization is likely to happen upon the formation due to the energy released by the H-atom-addition reaction or by H-atom tunnelling. Two different HCN(H)O isomers can be formed by an H atom addition to the H atom of the N atom of HCNO. Both of these reaction paths have high-energy barriers, *ca.* 60 and 90 kJ mol⁻¹. Furthermore, the energy of these products is much higher than that of the HCNOH isomers. Therefore, these reaction channels are expected to be closed at low temperatures. Finally, the H atom addition to the C atom of HCNO, leading to H₂CNO, has a very low-energy computed barrier, around 1 kJ mol⁻¹. Considering only the PES, this reaction channel should be permeable by H-atom tunnelling even at the temperature of our experiments, at 3.1 K.

Since, according to the above arguments, the HCN(H)O isomers are not expected to be formed, furthermore, all the possible H-atom-addition products of HCN(H)O isomers are also expected to have high energies, these structures are not considered in the further discussion. The H atom addition to the C atom of the HCNOH isomers, and to the O atom of H₂CNO lead to *syn*- and *anti*-H₂CNOH. These reactions, being radical–radical recombination process, are barrierless, and can proceed at low temperatures. For simplicity, in Fig. 2 only *anti*-H₂CNOH is shown. As was mentioned only this form was identified in low-temperature matrices (Heikkilä et al. 1999) and as it will be discussed we could identify only this isomer in our experiments. This can be rationalized by the computed barrier height of 14.9 kJ mol⁻¹ from the *syn* to the more stable *anti* form. The half-life of the isomerization by the rotation of the OH group

Table 1. The relative energies corresponding to the steps of H-atom-addition and H-atom-abstraction reactions together with the relative energies of the TSs. Relative energies in kJ mol⁻¹ are computed at the B3LYP/cc-pVTZ level of theory. The energies are given both without and with ZPVE correction.

	ΔE (kJ mol ⁻¹)	$\Delta E + \text{ZPVE}$ (kJ mol ⁻¹)
H-atom-addition reactions		
CNO + 5 H	0.0	0.0
HCNO + 4 H	-451.1	-422.5
TS ₁ + 3 H	-451.3	-421.2
H ₂ CNO + 3 H	-723.5	-664.7
TS ₂ + 3 H	-370.6	-339.9
<i>a,c</i> -HCNOH + 3 H	-603.7	-552.4
TS ₃ + 3 H	-341.6	-310.8
<i>a,t</i> -HCNOH + 3 H	-615.5	-559.5
TS ₄ + 3 H	-409.7	-378.9
<i>s,c</i> -HCNOH + 3 H	-583.3	-532.2
TS ₅ + 3 H	-421.6	-389.1
<i>s,t</i> -HCNOH + 3 H	-605.9	-551.0
TS ₆ + 3 H	-361.2	-349.3
<i>c</i> -HCN(H)O + 3 H	-521.7	-466.5
TS ₇ + 3 H	-393.9	-359.2
<i>t</i> -HCN(H)O + 3 H	-512.7	-457.8
<i>a</i> -H ₂ CNOH + 2 H	-1074.5	-983.4
<i>s</i> -H ₂ CNOH + 2 H	-1054.8	-962.6
TS ₈ + H	-1064.7	-970.2
<i>a</i> -H ₂ CN(H)OH + H	-1209.3	-1095.7
TS ₉ + H	-1073.6	-977.9
<i>a</i> -H ₃ CNOH + H	-1277.3	-1158.8
TS ₁₀ + H	-1031.8	-937.9
H ₂ CN + H ₂ O + H	-1320.7	-1222.2
H ₃ CN(H)OH	-1625.9	-1472.6
H-atom-abstraction reactions		
H ₃ CN(H)OH + 5 H	0.0	0.0
TS ₁₁ + 4 H	22.8	13.6
<i>a</i> -H ₂ CN(H)OH + 4 H + H ₂	-44.4	-58.2
TS ₁₂ + 4 H	4.5	4.7
<i>a</i> -H ₃ CNOH + 4 H + H ₂	-112.3	-121.3
TS ₁₃ + 4 H	3.4	1.0
H ₃ CN(H)O + 4 H + H ₂	-142.2	-148.1
TS ₁₄ + 4 H	42.6	34.3
<i>s</i> -H ₂ CN(H)OH + 4 H + H ₂	-41.3	-51.9
TS ₁₅ + 4 H	42.6	38.4
<i>s</i> -H ₃ CNOH + 4 H + H ₂	-92.2	-103.3
<i>a</i> -H ₂ CNOH + 3 H + 2 H ₂	-370.4	-381.0
<i>s</i> -H ₂ CNOH + 3 H + 2 H ₂	-361.8	-350.7
TS ₁₆ + 2 H + 2 H ₂	-350.4	-370.3
H ₂ CNO + 2 H + 3 H ₂	-480.4	-497.3
TS ₁₇ + 2 H + 2 H ₂	-322.9	-342.4
<i>a,c</i> -HCNOH + 2 H + 3 H ₂	-360.6	-385.0
TS ₁₈ + 2 H + 2 H ₂	-335.1	-353.8
<i>a,t</i> -HCNOH + 2 H + 3 H ₂	-372.3	-392.2
HCNO + H + 4 H ₂	-668.9	-690.1
TS ₁₉ + 4 H ₂	-628.6	-655.9
CNO + 5 H ₂	-678.7	-679.5

with an H-atom tunnelling mechanism is expected to be well below a second in an Ar matrix (Bazsó, Magyarfalvi & Tarczay 2012), and it is expected to be even faster in a *para*-H₂ matrix (Góbi et al. 2022). Another possible product of the H₂CNO + H reaction is H₃CNO. Although this reaction is also barrierless, it would lead to a high-energy product; therefore, its formation is less favoured than that of *anti*-H₂CNOH.

The addition of an H atom to the O atom of *anti*-H₂CNOH leads to the breaking of the NO bond, and to the formation of H₂CN and H₂O. This reaction has a barrier of 159.9 kJ mol⁻¹ at the B3LYP/cc-pVTZ level of theory with ZPVE correction. Therefore, it is not expected to proceed at a low temperature. At the same level of theory, the barrier height of the reaction leading to *anti*-H₂CN(H)OH is 13.2 kJ mol⁻¹, which might be crossed via H-atom tunnelling at low temperatures. The product of the *anti*-H₂CNOH + H reaction with the lowest energy barrier is *anti*-H₃CNOH, computed to be only 5.5 kJ mol⁻¹. Therefore, the formation of this species is highly expected.

The final [5H, C, N, O] product is N-methylhydroxylamine (H₃CN(H)OH), which can be formed from H₃CNOH and an H atom in a barrierless radical–radical recombination process.

An H atom can abstract an H atom from H₃CN(H)OH forming either *anti*- and *syn*-H₃CNOH and H₂ or *anti*- and *syn*-H₂CN(H)OH and H₂, and also H₃CN(H)O and H₂. These reactions have computed barrier heights of 4.7, 38.4, 13.6, 34.3, and 1.0 kJ mol⁻¹, respectively (Fig. 3 and Table 1). These values predict that all of these channels are likely to open by H-atom tunnelling at low temperature. Both the H-atom abstraction from the H₃ group of *anti*- and *syn*-H₃CNOH or from the NH group of *anti*- and *syn*-H₂CN(H)OH are barrierless, and lead to *anti*- and *syn*-H₂CNOH. As discussed above, even if *syn*-H₂CNOH would initially form, it is rapidly converted to *anti*-H₂CNOH.

The formation of [2H, C, N, O] isomers from *anti*-H₂CNOH have barriers in every case but it is the smallest for H₂CNO. It is computed to be 10.7 kJ mol⁻¹, when ZPVE is taken into account. As has been already mentioned before, H₂CNO is the most stable [2H, C, N, O] isomer. This implies that the H₂CNO should be the most abundant [2H, C, N, O] isomer formed by an H-atom-abstraction reaction. The formation of HCNO from any [2H, C, N, O] isomers is barrierless. Thus, these reactions are also expected to proceed at low temperature.

Finally, the H-atom-abstraction reaction from HCNO, leading to CNO radical and H₂ is an endoergic reaction and therefore it cannot proceed at low temperature.

3.2 Experiments with *anti*-H₂CNOH

The IR spectra of *anti*-H₂CNOH in *para*-H₂ matrix after the deposition are shown in Figs 4 and 5. The most intense bands of *anti*-H₂CNOH can be found in the spectra at 3631.7, 892.8, and 1317.5 cm⁻¹. These values agree well with the previous measurements (Table 2) in Ar matrix and in gas phase (Bannai et al. 1996; Heikkilä et al. 1999). After completing the deposition, H atoms were generated and their reactions with *anti*-H₂CNOH were examined. As it is discussed below, both H-atom-abstraction and H-atom-addition reactions were observed.

In agreement with the computational predictions, H-atom-abstraction reactions led to the formation of H₂CNO and HCNO as it is shown in Figs 4 and 5. The H₂CNO radical is formed directly from *anti*-H₂CNOH, and HCNO from H₂CNO. H₂CNO was investigated earlier in Ar matrix (McCluskey & Frei 1993), whereas HCNO in Ar matrix and in gas phase (Bondybey et al. 1982; Teles et al. 1989). The assignments of this work are in good agreement with the literature data (see Tables 3 and 4). The bands of H₂CNO are observed at 1662.6, 1197.7, 1107.9, and 789.8 cm⁻¹, respectively, while those of HCNO at 3326.1, 2194.6, and 1247.1 cm⁻¹.

The assignments can be further confirmed by the qualitative behaviour of the bands during each phase of the processes of the experiment (see Figs 4 and 5). Due to the IR irradiation of the light source of the IR spectrometer a small portion of H atoms are already generated from the reaction with Cl atoms during the

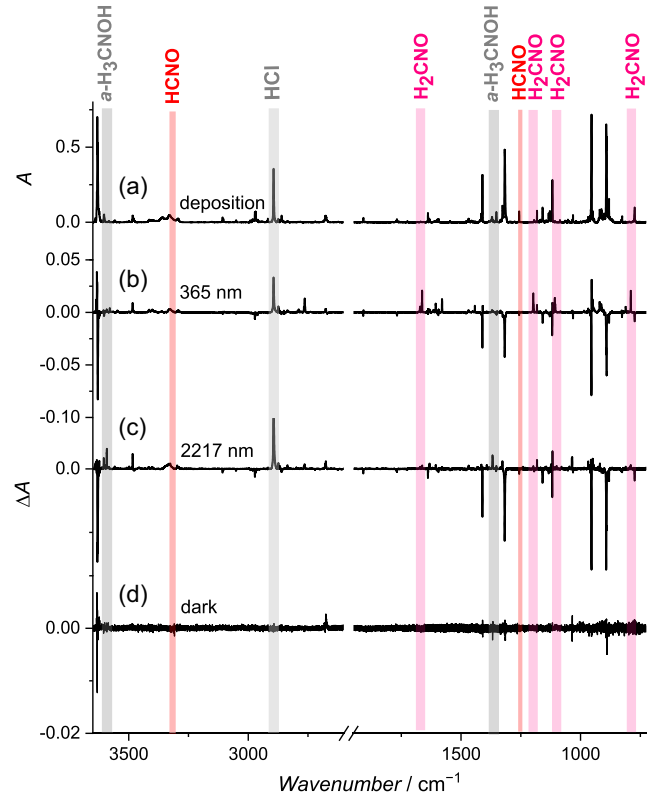


Figure 4. Overview spectra of the experiment with *anti*-H₂CNOH at 3.1 K. (a) The MIR spectrum recorded after the deposition of *para*-H₂ matrix containing *anti*-H₂CNOH and Cl₂ at 3.1 K. (b) The difference spectrum corresponding to the 365 nm irradiation (flux (Φ) = 1.6×10^{15} cm⁻² s⁻¹). (c) The difference spectrum corresponding to the 2217 nm irradiation (Φ = 6.9×10^{16} cm⁻² s⁻¹). (d) The difference spectrum corresponding to the dark process. The difference spectra were obtained by subtracting the MIR spectrum recorded before from the one recorded after the given experimental step.

365 nm irradiation. The bands of the primary product, H₂CNO, start to increase during this process. As shown in Fig. 6 its mixing ratio further increased during the H atom generation by 2217 nm irradiation. Upon the dark process, i.e. the H atom reaction in low-temperature conditions, its mixing ratio was constant or very slightly increased in the first 3 h, then it started to decrease until the end of the experiment.

In contrast to this, the intensity of the HCNO bands increased very slightly during the 365 nm irradiation (see Figs 4 and 5), then significantly increased during the 2217 nm irradiation, and slowly increased during the whole dark process (see Fig. 6). The mixing ratio of *anti*-H₂CNOH gradually decreased upon each process (see Figs 4, 5, and 6).

It is important to note that the bands assigned to HCNO and H₂CNO are absent in the blank experiments when the same irradiation sequence was used but the matrix was not doped with Cl₂, hence H atoms are not generated. (See Fig. S1 and Tables S3 and S7 in the Supporting Information.)

Another peak arises during the H atom reactions at 1241.4 cm⁻¹. Its intensity increased in all phases of the experiment, i.e. during the 365 and 2217 nm irradiations and in the dark. According to the quantum chemical computations, this band might belong to the *anti*,*cis*-HCNOH radical (Table S34 in the Supporting Information), which may be generated from *anti*-H₂CNOH by H-atom-abstraction

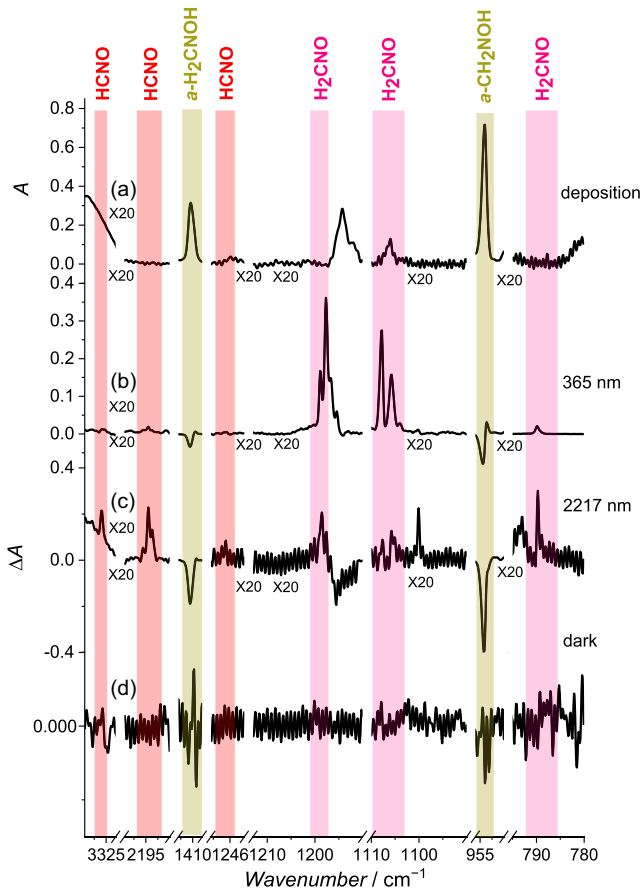


Figure 5. Spectra of the experiment with *anti*-H₂CNOH at 3.1 K enlarged at some key spectral bands. (a) The MIR spectrum recorded after the deposition of *para*-H₂ matrix containing *anti*-H₂CNOH and Cl₂ at 3.1 K. (b) The difference spectrum corresponding to the 365 nm irradiation ($\Phi = 1.6 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$). (c) The difference spectrum corresponding to the 2217 nm irradiation ($\Phi = 6.9 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$). (d) The difference spectrum corresponding to the dark process. The difference spectra were obtained by subtracting the MIR spectrum recorded before from the one recorded after the given experimental step.

reaction. However, the vibrational mode that can be assigned to this band is not the most intense one of *anti*,*cis*-HCNOH and no other bands could be assigned to this species leaving this assignment tentative only.

Besides the H-atom-abstraction reactions, an H-atom-addition reaction also takes place, leading to the formation of *anti*-H₃CNOH. Its bands appeared in the spectra at 3591.6, 2878.5, 1368.2, 1079.7, and 929.4 cm⁻¹, respectively. The experimental band positions agree well with the computationally obtained vibrational frequencies of this radical, as it is shown in Table 5. As was discussed in the previous section, *anti*-H₃CNOH can be formed from *anti*-H₂CNOH via a low-barrier H-atom tunnelling process. Fig. 4 also implies that similarly to HCNO, the band intensities of *anti*-H₃CNOH increased moderately already during the 365 nm irradiation, then increased more profoundly during the 2217 nm irradiation, and further increased in the dark. Importantly, *anti*-H₃CNOH was not detected in the blank experiments (Table S28 and Fig. S1 in the Supporting Information). Although the fully hydrogenated H₃CN(H)OH can be formed without an energy barrier, this molecule was not identified in *para*-H₂ matrix. This might be explained by the faster H-atom

Table 2. Comparison of experimental vibrational wavenumbers and IR intensities of *anti*-H₂CNOH isolated in solid Ar matrix, in gas phase and isolated in solid *para*-H₂ matrix.

Ar matrix ^a $\tilde{\nu}$ (cm ⁻¹)	<i>anti</i> -H ₂ CNOH		
	Gas phase ^b $\tilde{\nu}$ (cm ⁻¹)	<i>para</i> -H ₂ matrix $\tilde{\nu}$ (cm ⁻¹) ^c	<i>I</i> ^{c, d}
3620	3650	3631.7	100
3104	3110	3104.1	0.6
2976	2974	2969.4	2
1624	1640	1638.5	3
1408	1411	1410.5	14
1313	1319	1317.5	63
1151	1157	1159.0	7
954	953	954.1	35
886	893	892.8	76
880	-	881.1	2
774	773	773.7	6
770	-	771.5	-
526	530	-	-
-	398	-	-

Notes.^aHeikkilä et al. (1999)

^bBannai et al. (1996)

^cThis work, starting from *anti*-H₂CNOH.

^dRelative integrated intensity, normalized to the most intense band.

Table 3. Comparison of experimental vibrational wavenumbers and IR intensities of H₂CNO isolated in solid Ar matrix and isolated in solid *para*-H₂ matrix.

H ₂ CNO					
Ar matrix ^a $\tilde{\nu}$ (cm ⁻¹)	<i>I</i> ^b	$\tilde{\nu}$ (cm ⁻¹) ^c	<i>para</i> -H ₂ matrix		<i>I</i> ^{b, d}
			<i>I</i> ^{b, c}	$\tilde{\nu}$ (cm ⁻¹) ^d	
1664	100	1662.8	50	1662.6	41
1197	72	1197.7	100	1197.7	100
1106	48	1108.0	13	1107.9	12
793	37	789.6	-*	789.8	35

Notes.*Overlaps with the bands of other species.

^aMcCluskey & Frei (1993)

^bRelative integrated intensity, normalized to the most intense band.

^cThis work, starting from HCNO

^dThis work, starting from *anti*-H₂CNOH.

Table 4. Comparison of experimental vibrational wavenumbers and IR intensities of HCNO isolated in solid Ar matrix, in gas phase and isolated in solid *para*-H₂ matrix.

HCNO						
Ar matrix ^a $\tilde{\nu}$ (cm ⁻¹)	<i>I</i> ^c	Gas phase ^b		<i>para</i> -H ₂ matrix		<i>I</i> ^{c, e}
		$\tilde{\nu}$ (cm ⁻¹)	$\tilde{\nu}^d$ (cm ⁻¹)	<i>I</i> ^{b, d}	$\tilde{\nu}^e$ (cm ⁻¹)	
3416	14	-	-	-	-	-
3317	61	3336	3325.9	96	3326.1	33
2480	6	2498	-	-	-	-
2193	100	2196	2194.7	100	2194.6	100
1244	34	1254	1247.2	43	1247.1	25
567	37	542	-	-	-	-
538	5	538	-	-	-	-
537	4	-	-	-	-	-
243	14	225	-	-	-	-

Notes.^aTeles et al. (1989)

^bBondybey et al. (1982)

^cRelative integrated intensity, normalized to the most intense band.

^dThis work, starting from HCNO.

^eThis work, starting from *anti*-H₂CNOH.

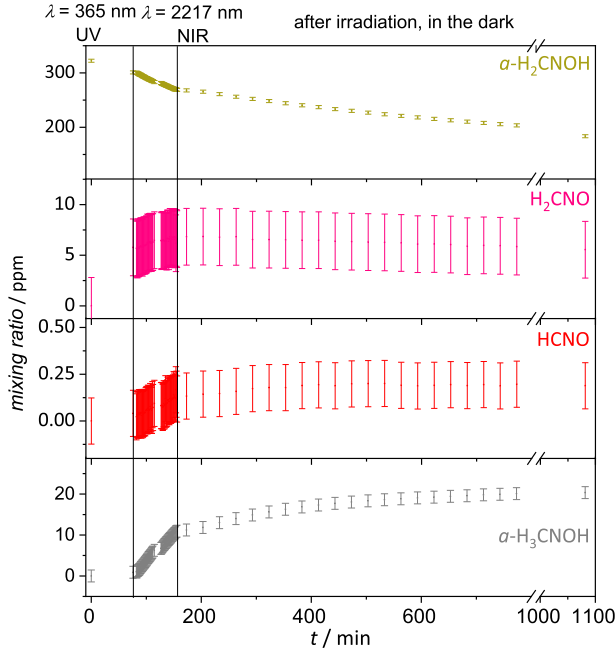


Figure 6. Temporal evolution of the mixing ratio of *anti*-H₂CNOH, H₂CNO, HCNO and *anti*-H₃CNOH in the experiment starting from *anti*-H₂CNOH. The mixing ratio of the H atoms was 640 ± 110 ppm.

Table 5. Comparison of experimental vibrational wavenumbers and IR intensities of *anti*-H₃CNOH isolated in solid *para*-H₂ matrix and those computed at the CCSD(T)/cc-pVTZ level of theory with anharmonic correction at the B3LYP/cc-pVTZ level of theory.

$\tilde{\nu}$ (cm ⁻¹)	<i>anti</i> -H ₃ CNOH		$\tilde{\nu}$ (cm ⁻¹)	I^b, c
	Computed ^a	I^b		
3641.5	54		3591.6	100
2967.7	15		—	—
2888.6	24		2878.5	4
2866.4	16		—	—
1460.9	0.2		—	—
1446.0	7		—	—
1394.8	8		—	—
1393.5	49		1368.2	65
1148.5	5		—	—
1034.9	61		1079.7	7
1019.5	4		—	—
924.9	21		929.4	3
624.1	100		—	—
492.4	10		—	—
216.8	0.2		—	—

Notes. ^aComputed at the CCSD(T)/cc-pVTZ level of theory with the anharmonic corrections.

^bRelative integrated intensity, normalized to the most intense band.

^cThis work, starting from *anti*-H₂CNOH.

abstraction of *anti*-H₃CNOH, which is also barrierless (see Fig. 3), which leads back to the formation of *anti*-H₂CNOH.

Finally, a further product, a small amount of NH₃ was formed. The bands of NH₃ can be seen in the spectra at 1631.9 and 968.3 cm⁻¹, respectively, which match well with the measured vibrational frequencies in Ar matrix and in the gas phase (Table S35 in the Supplementary Information) (Shimanouchi et al. 1972; Bossa et al. 2008). The quantity of NH₃ increased during the 365

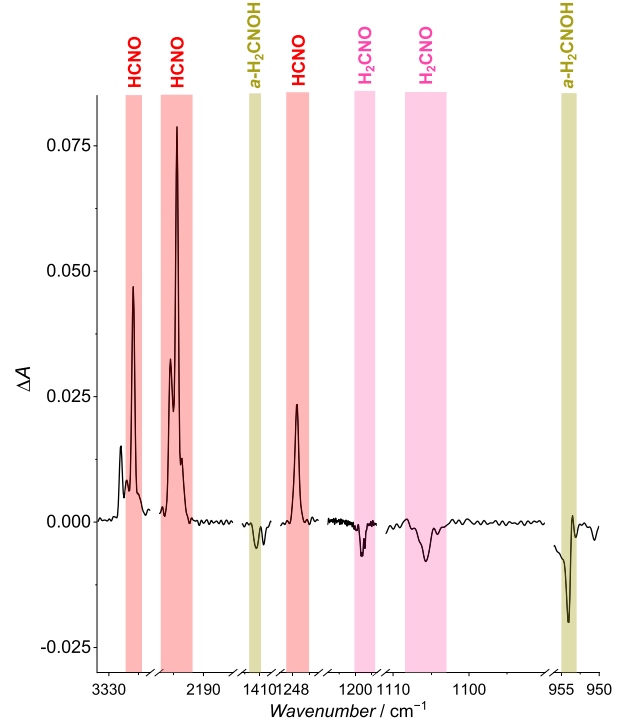


Figure 7. Difference spectrum of the secondary 270 nm UV photolysis ($\Phi = 1.2 \times 10^{15}$ cm⁻² s⁻¹) of the *para*-H₂ matrix containing *anti*-H₂CNOH and its reaction products with H atoms at 3.1 K. The difference spectrum was obtained by subtracting the MIR spectrum recorded before the irradiation from the MIR spectrum recorded after the irradiation.

and the 2217 nm irradiation but barely changed when the sample was left in the dark. It might be generated from formaldoxime complexed with contaminant water molecules by laser-irradiation activation.

As can be seen in Fig. 6, the sum of the change of the mixing ratios of the different species is not zero. It can be explained partly by the uncertainties of the computed anharmonic IR intensities used for the determination of mixing ratios, and partly by the possible sublimation of the matrix, especially during the 2217 nm irradiation. Furthermore, there might be other, unidentified minor products.

The assignments were further confirmed by a subsequent 270 nm irradiation. Upon this secondary UV photolysis, the bands assigned to the same species showed the same qualitative behaviour; the intensity of the bands of *anti*-H₂CNOH and H₂CNO decreased, while the intensity of the HCNO bands increased, as it is shown in Fig. 7. Besides the main product HCNO, other molecules, namely HNCO, HCN, H₂CN, and HNC, were also formed. The assignment of these species is in great agreement with previous experiments in *para*-H₂ (in the case of HNCO) or in Ar matrix and in the gas phase (in the case of HCN, H₂CN and HNC) as it is shown in Table 6 and in Tables S36, S37, and S38 in the Supplementary Information.

3.3 Experiments with HCNO

As it was described in Section 2, HCNO was prepared by the 220 nm photodecomposition of 1,2,5-oxadiazole in *para*-H₂ matrix. The reaction scheme is presented in Fig. 8. Besides HCNO, this photolysis generated other [H, C, N, O] isomers, HCN, and a small amount of NH₃ (Fig. 9). The assignments of the observed bands were in good agreement with previous experiments, which studied the particles in *para*-H₂ matrix (in the case of HNCO) or in Ar

Table 6. Comparison of experimental vibrational wavenumbers and IR intensities of HNCO isolated in solid *para*-H₂ matrix.

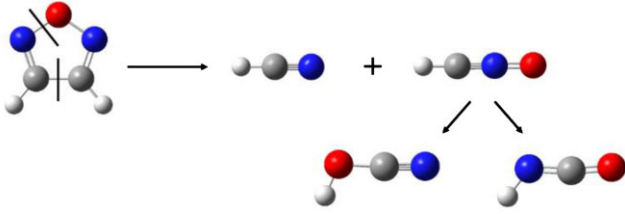
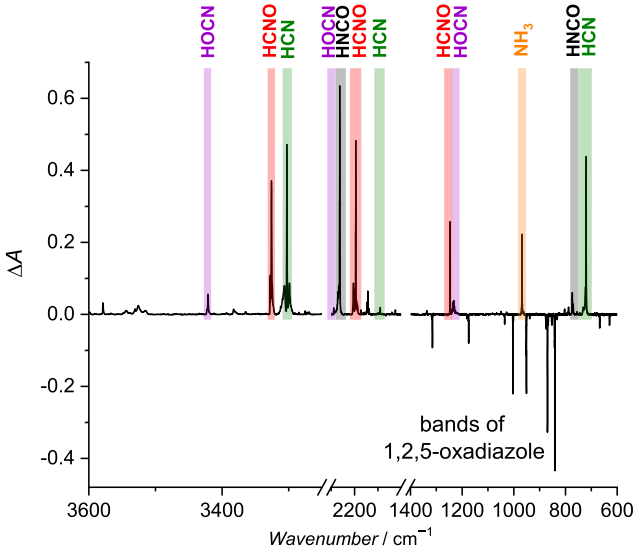
$\tilde{\nu}$ (cm ⁻¹) ^a	<i>I</i> ^{a, b}	HNCO <i>para</i> -H ₂ matrix		$\tilde{\nu}$ (cm ⁻¹) ^d	<i>I</i> ^{b, d}
		$\tilde{\nu}$ (cm ⁻¹) ^c	<i>I</i> ^{b, c}		
3536	2	—	—	—	—
2264	100	2263.2	100	2263.2	100
2263					
773	19	773.9	12	—	—
770					

Notes.^aHaupa et al. (2019a)

^bRelative integrated intensity, normalized to the most intense band.

^cThis work, starting from HCNO.

^dThis work, starting from *anti*-H₂CNOH.


Figure 8. The 220 nm photodecomposition of 1,2,5-oxadiazole and the formation of the [H, C, N, O] isomers.

Figure 9. Assignments of the products of the 220 nm UV photolysis of 1,2,5-oxadiazole in *para*-H₂ matrix at 3.1 K. The difference spectrum was obtained by subtracting the MIR spectrum recorded after the 220 nm irradiation ($\Phi = 1.2 \times 10^{14}$ cm⁻² s⁻¹) from the MIR spectrum recorded after the deposition of the *para*-H₂ matrix, which contained 1,2,5-oxadiazole and Cl₂. The negative bands of the spectrum are those of the 1,2,5-oxadiazole.

matrix and in the gas phase (in the case of HCNO, HOCN, HCN, and NH₃). The obtained band positions and intensities together with the assignments are listed for the [H, C, N, O] isomers in Tables 4, 6, and 7. The assignments for NH₃ and HCN are listed in Tables S35 and S36 of the Supporting information. As was shown before (Keresztes et al. 2020), HNCO and HOCN isomers are the photoisomerization products of the primary product, HCNO, whereas HCN is the by-product of the photodecomposition of 1,2,5-oxadiazole.

Table 7. Comparison of experimental vibrational wavenumbers and IR intensities of HOCN isolated in solid Ar matrix, in the gas phase and isolated in solid *para*-H₂ matrix.

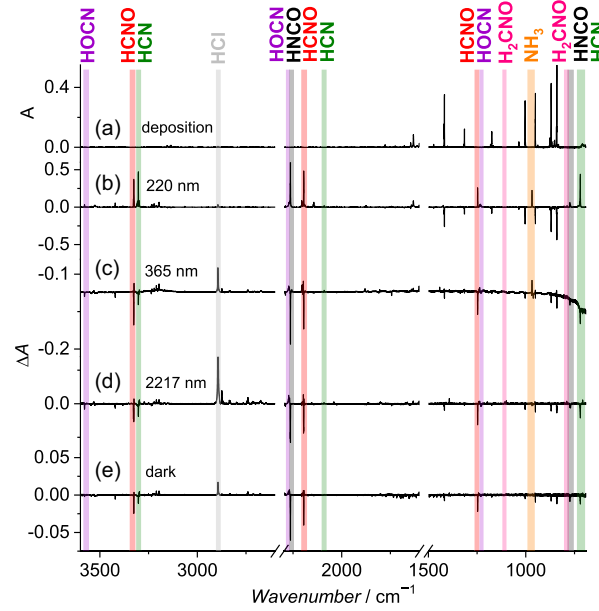
Ar matrix ^a		HOCN		
$\tilde{\nu}$ (cm ⁻¹)	<i>I</i>	Gas phase ^b $\tilde{\nu}$ (cm ⁻¹)	<i>para</i> -H ₂ matrix $\tilde{\nu}^c$ (cm ⁻¹)	<i>I</i> ^{c, d}
3570	s	—	3567.3	27
2286	vs	2302	2289.0	100
1228	s	—	1232.2	90
1081	m	—	—	—

Notes.^aJacox & Milligan (1964)

^bSu et al. (2000)

^cThis work, starting from HCNO.

^dRelative integrated intensity, normalized to the most intense band.


Figure 10. Overview spectra of the experiment with HCNO generated from 1,2,5-oxadiazole at 3.1 K. (a) The MIR spectrum recorded after the deposition of *para*-H₂ matrix containing *anti*-H₂CNOH and Cl₂ at 3.1 K. (b) The difference spectrum corresponding to the 220 nm irradiation ($\Phi = 1.2 \times 10^{14}$ cm⁻² s⁻¹). (c) The difference spectrum corresponding to the 365 nm irradiation ($\Phi = 1.6 \times 10^{15}$ cm⁻² s⁻¹). (d) The difference spectrum corresponding to the 2217 nm irradiation ($\Phi = 6.0 \times 10^{16}$ cm⁻² s⁻¹). (e) The difference spectrum corresponding to the dark process. The difference spectra were obtained by subtracting the MIR spectrum recorded before from the one recorded after the given experimental step.

Similarly to the experiments performed with *anti*-H₂CNOH, H atoms were generated by subsequent 365 and 2217 nm irradiations of a Cl₂-doped matrix (see details in Section 2) and the reactions of H atoms were followed by IR spectroscopy. Since the H-atom-abstraction reactions of the [H, C, N, O] isomers and HCN are endoergic and cannot proceed in a 3.1 K matrix, only the H-atom-addition reactions need to be considered in this experiment.

As can be seen in Figs 10 and 11, in line with the expectation based on the quantum chemical computations, the reactions of H atoms with HCNO yield H₂CNO. The intensity of the HCNO bands decrease during the 365 and 2217 nm photolyses and in the dark, those of H₂CNO increase monotonically (Fig. 12). This radical is observed in the spectra at wavenumbers of 1662.8, 1197.7, 1108.0,

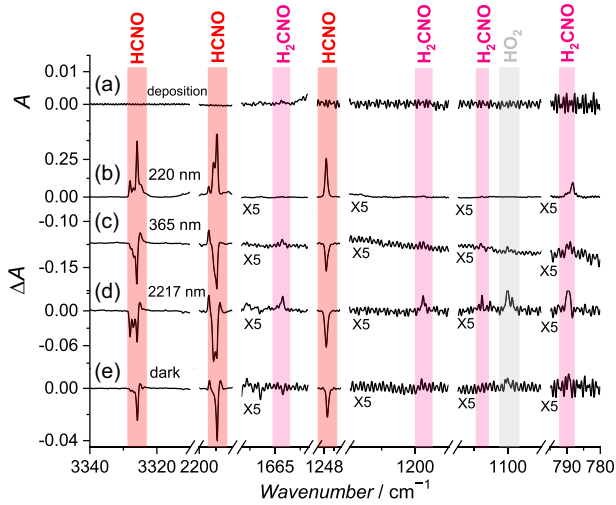


Figure 11. Spectra of the experiment with HCNO generated from 1,2,5-oxadiazole at 3.1 K enlarged at some key spectral bands. (a) The MIR spectrum recorded after the deposition of *para*-H₂ matrix containing *anti*-H₂CNOH and Cl₂ at 3.1 K. (b) The difference spectrum corresponding to the 220 nm irradiation ($\Phi = 1.2 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$). (c) The difference spectrum corresponding to the 365 nm irradiation ($\Phi = 1.6 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$). (d) The difference spectrum corresponding to the 2217 nm irradiation ($\Phi = 6.0 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$). (e) The difference spectrum corresponding to the dark process. The difference spectra were obtained by subtracting the MIR spectrum recorded before from the one recorded after the given experimental step. HO₂ is the product of H atoms and O₂ contamination.

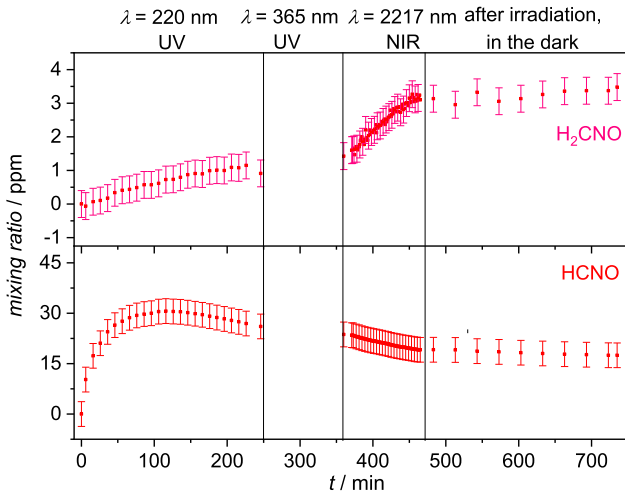


Figure 12. Temporal evolution of the mixing ratio of HCNO and H₂CNO in the experiment starting from HCNO. The mixing ratio of the H atoms was $810 \pm 140 \text{ ppm}$.

and 789.6 cm^{-1} , respectively. These are in good accordance with the band positions of H₂CNO observed in the experiments carried out with *anti*-H₂CNOH (Table 3).

The H-atom-addition process of HNCO has already been examined indirectly (Haupa et al. 2019a). In that study, the reaction of partially deuterated formamide, D₂NC(H)O with H atoms resulted in the formation of DNCO, HNCO, H₂NCO, HDNCO, HDNC(H)O, and H₂NC(H)O. The H-D exchange proved that HNCO and DNCO can react with H atoms in an addition reaction. In this study, we see direct evidence of this reaction, as after generating H atoms, we could observe the most intense band of H₂NCO at 1809.9 cm^{-1} (Table 8).

Table 8. Comparison of experimental vibrational wavenumbers and IR intensities of H₂NCO isolated in solid *para*-H₂ matrix.

$\tilde{\nu} \text{ (cm}^{-1}\text{)}^a$	H ₂ NCO <i>para</i> -H ₂ matrix		$I^{b,c}$
	$I^{a,b}$	$\tilde{\nu} \text{ (cm}^{-1}\text{)}^c$	
3542.9	22	—	—
3392.7	4	—	—
1809.5	100	1809.9	100
1565.9	53	—	—
1211.2	15	—	—
1210.8	—	—	—
579.7	<1	—	—

Notes. ^aHaupa et al. (2019a)

^bRelative integrated intensity, normalized to the most intense band.

^cThis work, starting from HCNO.

By varying the time of the initial 220 nm photolysis, the amount of the generated HCNO and HNCO isomers could be varied greatly. However, in all experiments the quantity of HOCN was almost completely negligible compared to the other two isomers. Therefore, even if HOCN reacts with H atoms, these products were below the detection limit.

The assignments of H₂CNO and H₂NCO are further confirmed by the fact that in the blank experiments, when H atoms are not generated, their bands did not appear in the spectra (Fig. S2 and Table S7 and S8 of the Supporting Information). They did not appear either in the experiments when the preliminary 220 nm UV photolysis was omitted (Fig. S3 of the Supporting Information), indicating that these bands cannot be assigned to the possible reaction products of H atoms with 1,2,5-oxadiazole. The bands which appeared in the spectra during the experiments without preliminary 220 nm UV photolysis are listed in Table S39 in the Supporting Information.

Although both the H₂CNO + H → H₂CNOH and the H₂NCO + H → H₂NC(H)O are barrierless recombination reactions, we were not able to identify any of the H₂CNOH and H₂NC(H)O isomers even in experiments with high H-atom mixing ratios. This indicates that the H-atom-abstraction reactions of H₂CNO and H₂NCO leading back to the formation of HCNO and HNCO, respectively, are faster than the H-atom-addition reactions of these radicals.

The assignments were further confirmed by a secondary 280 nm UV photolysis. As mentioned above, the different absorption bands of the same molecule show identical qualitative behaviour upon photolysis. Accordingly, the intensity of all the HCNO bands increased, whereas those of the H₂CNO decreased as shown in Fig. 13.

4 CONCLUSIONS

In this study, we took advantage of the *para*-H₂ matrix-isolation method to study the H-atom reactions of fulminic acid (HCNO) and *anti*-formaldoxime (*anti*-H₂CNOH). In agreement with the computational predictions, the experiments proved that both the H-atom-addition reaction with HCNO and the H-atom-abstraction reaction with formaldoxime proceed at low temperatures, and both of these reactions yield H₂CNO radical. Also in line with the computational predictions, H-atom-addition reaction also takes place with formaldoxime, leading to the formation of H₃CNOH radical. Both H₂CNO and H₃CNOH radicals can react with H atoms, either in a H-atom-addition reaction or in a H-atom-abstraction reaction. Although all these reactions are barrierless, the H-atom-addition reactions were undetected, revealing that the H-atom-abstraction reactions of these radicals are more effective. These experimentally observed reactions,

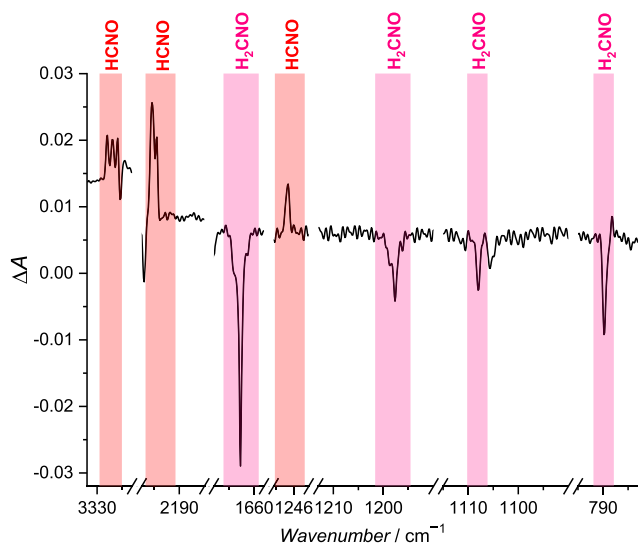


Figure 13. Difference spectrum of the secondary 280 nm UV photolysis ($\Phi = 2.0 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$) of the *para*-H₂ matrix containing HCNO and its reaction products with H atoms at 3.1 K. The difference spectrum was obtained by subtracting the MIR spectrum recorded before the irradiation from the MIR spectrum recorded after the irradiation.

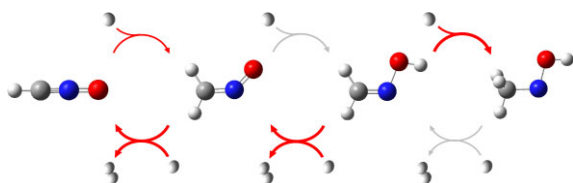


Figure 14. Tricyclic H-atom-addition and H-atom-abstraction mechanism involving HCNO and formaldoxime. The red arrows show the experimentally observed reactions at 3.1 K, and the grey arrows are those barrierless reactions which were not directly observed.

together with the unobserved but presumably feasible radical–radical recombination reactions, form a tricyclic reaction mechanism as shown in Fig. 14. Therefore, in the presence of H atoms and under quasi-equilibrium conditions, the abundance of formaldoxime in dark molecular clouds is expected to be lower than that of HCNO.

In addition, we have also observed the H-atom-addition reaction of isocyanic acid (HNCO) yielding H₂NCO radical. Similarly to the case of HCNO, we did not observe the product of the second H atom addition, formamide (H₂NC(H)O). These observations are in agreement with former laboratory studies (Noble et al. 2015; Haupa et al. 2019a). Since the H-atom-addition reaction of H₂NCO radical was formerly proved by H/D replacement, it can be concluded that among the barrierless H-atom-addition reactions and H-atom-abstraction reactions, the latter is more effective in this case, too.

Furthermore, this study together with former results (Haupa et al. 2019a; Schneiker et al. 2022) suggest that interstellar complex organic molecules (iCOMs) can simultaneously participate both in H-atom-addition and H-atom-abstraction reactions, forming cyclic mechanisms in which H₂ are produced from H atoms. Therefore, iCOMs might be common catalysts in interstellar H₂ formation.

ACKNOWLEDGEMENTS

This research was funded by the Lendület program of the Hungarian Academy of Sciences. The work was also supported by the Hungarian Scientific Research Fund (OTKA K143196) and by ELTE Institutional Excellence Program (TKP2020-IKA-05). SG was supported by the ‘Bolyai Ösztöndíj’ of the Hungarian Academy of Sciences. BK was supported by the ‘ÚNKP-21-2 and 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.

DATA AVAILABILITY

The data underlying this article are available in the article and in its online supplementary material. The IR spectra underlying this article can be requested from the corresponding author.

REFERENCES

- Balabanoff M. E., Ruzi M., Anderson D. T., 2018, *Phys. Chem. Chem. Phys.*, 20, 422
- Bannai R. A., Duxbury G., 1994, *J. Opt. Soc. Am. B*, 11, 170
- Bannai R. A., Duxbury G., Ritchie G., Klee S., 1996, *J. Mol. Spectr.*, 178, 84
- Bazsó G., Magyarfalvi G., Tarczay G., 2012, *J. Phys. Chem. A*, 116, 10539
- Bazsó G., Csonka I. P., Góbi S., Tarczay G., 2021, *Rev. Sci. Instr.*, 92, 124104
- Bondybey V. E., English J. H., Weldon Mathews C., Contolini R. J., 1982, *J. Mol. Spectr.*, 92, 431
- Bossa J.-B., Duvernay F., Theulé P., Borget F., Chiavassa T., 2008, *Chem. Phys.*, 354, 211
- Brünken S., Gottlieb C. A., McCarthy M. C., Thaddeus P., 2009, *ApJ*, 697, 880
- Brünken S., Belloche A., Martín S., Verheyen L., Menten K. M., 2010, *A&A*, 516, A109
- Duxbury G., 1988, *J. Mol. Spectr.*, 132, 393
- Duxbury G., Percival R. M., Devoy D., Mahmoud M. R. M., 1988, *J. Mol. Spectr.*, 132, 380
- Frisch M. J. et al., 2009, Gaussian 09 Revision A.2.
- Fushitani M., Momose T., 2003, *Low Temp. Phys.*, 29, 740
- Góbi S., Csonka I. P., Bazsó G., Tarczay G., 2021, *ACS Earth Space Chem.*, 5, 1180
- Góbi S., Ragupathy G., Bazsó G., Tarczay G., 2022, *Photochem.*, 2, 563
- Golec B., Mielke Z., 2007, *J. Mol. Struct.*, 844–845, 242
- Golec B., Grzegorzec J., Mielke Z., 2008, *Chem. Phys.*, 353, 13
- Golec B., Bil A., Mielke Z., 2009, *J. Phys. Chem. A*, 113, 9434
- Golec B., Mucha M., Sałdyka M., Barnes A., Mielke Z., 2015, *Spect. Acta Part A: Mol. Biomol. Spectr.*, 136, 68
- Haupa K. A., Tielens A. G. G. M., Lee Y.-P., 2017, *Phys. Chem. Chem. Phys.*, 19, 16169
- Haupa K. A., Tarczay G., Lee Y.-P., 2019a, *J. Am. Chem. Soc.*, 141, 11614
- Haupa K. A., Strom A. I., Anderson D. T., Lee Y.-P., 2019b, *J. Chem. Phys.*, 151, 234302
- Haupa K. A., Ong W.-S., Lee Y.-P., 2020, *Phys. Chem. Chem. Phys.*, 22, 6192
- Haupa K. A., Joshi P. R., Lee Y.-P., 2022, *J. Chin. Chem. Soc.*, 69, 1159
- Heikkilä A., Pettersson M., Lundell J., Khriachtchev L., Räsänen M., 1999, *J. Phys. Chem. A*, 103, 2945
- Jacox M. E., Milligan D. E., 1964, *J. Chem. Phys.*, 40, 2457
- Joshi P. R., Lee Y.-P., 2022, *Commun. Chem.*, 5, 1
- Jusuf A., Tan T. L., Wu Q. Y., 2022, *J. Mol. Spectr.*, 387, 111665
- Kaushik V. K., Takagi K., 1978, *J. Phys. Soc. Jap.*, 45, 1975
- Keresztes B., Csonka I. P., Lajgút G. G., Bazsó G., Tarczay G., 2020, *J. Mol. Struct.*, 1219, 128535
- Klesing A., Sutter D. H., 1990, *Z. Nat.forsch. A*, 45, 817
- Lattalais M., Pauzat F., Ellinger Y., Ceccarelli C., 2009, *ApJ*, 696, L133

- Lattalais M., Pauzat F., Ellinger Y., Ceccarelli C., 2015, *A&A*, 578, A62
- Lee C.-F., Codella C., Ceccarelli C., López-Sepulcre A., 2022, *ApJ*, 937, 10
- Levine I. N., 1962, *J. Mol. Spect.*, 8, 276
- Levine I. N., 1963, *J. Chem. Phys.*, 38, 2326
- López-Sepulcre A. et al., 2015, *MNRAS*, 449, 2438
- Marcelino N., Cernicharo J., Tercero B., Roueff E., 2009, *ApJ*, 690, L27
- Marcelino N., Brünken S., Cernicharo J., Quan D., Roueff E., Herbst E., Thaddeus P., 2010, *A&A*, 516, A105
- Matthews D. A. et al., 2020, *J. Chem. Phys.*, 152, 214108
- McCluskey M., Frei H., 1993, *J. Phys. Chem.*, 97, 5204
- Mladenović M., Lewerenz M., McCarthy M. C., Thaddeus P., 2009, *J. Chem. Phys.*, 131, 174308
- Noble J. A. et al., 2015, *A&A*, 576, A91
- Pillai M. G. K., 1962, *J. Phys. Chem.*, 66, 179
- Quan D., Herbst E., Osamura Y., Roueff E., 2010, *ApJ*, 725, 2101
- Rubin R. H., Swenson G. W., Jr, Benson R. C., Tigelaar H. L., Flygare W. H., 1971, *ApJ*, 169, L39
- Rubin R. H., Benson R. C., Tigelaar H. L., Flygare W. H., 1972, in *Microwave detection of interstellar formamide (Formamide rotational transition microwave emission detection in interstellar medium in Sgr B 2 and Sgr A direction)*. Colloque International d'Astrophysique, 17 th, Liege, Belgium, June 28–30, 1971.) Societe Royale des Sciences de Liege, Memoires, Vol. 3, p. 471
- Ruzi M., Anderson D. T., 2015, *J. Phys. Chem. A*, 119, 12270
- Schneiker A., Góbi S., Joshi P. R., Bazsó G., Lee Y.-P., Tarczay G., 2021, *J. Phys. Chem. Letters*, 12, 6744
- Schneiker A., Ragupathy G., Bazsó G., Tarczay G., 2022, *J. Phys. Chem. A*, 126, 2832
- Shimanouchi T., et al., 1972, *Tables of molecular vibrational frequencies, NSRDS-NBS 39 Vol. 1*. National Bureau of Standards, Washington, DC
- Snyder L. E., Buhl D., 1972, *ApJ*, 177, 619
- Stanton J. F., Gauss J., Cheng L., Harding M. E., Matthews D. A., Szalay P. G., 2020, *CFOUR*, Coupled-Cluster techniques for Computational Chemistry, a quantum-chemical program package.
- Su H., Kong F., Chen B., Huang M.-B., Liu Y., 2000, *J. Chem. Phys.*, 113, 1885
- Suhasaria T., Mennella V., 2020, *A&A*, 641, A88
- Tan T. L., Jusuf A., Wu Q. Y., 2021, *J. Mol. Spect.*, 380, 111499
- Tarczay G., Haupa K., Lee Y.-P., 2019, *Proc. Int. Astron. Un.*, 15, 394
- Teles J. H., Maier G., Andes Hess B., Jr, Schaad L. J., Winnewisser M., Winnewisser B. P., 1989, *Chem. Ber.*, 122, 753
- Tsai S.-Y., Haupa K. A., Lee Y.-P., 2022, *J. Am. Chem. Soc.*, 144, 12339
- Tsuge M., Lee Y.-P., 2020, in *Gupta V., Ozaki Y.eds, Molecular and Laser Spectroscopy, Advances and Applications, Vol. 2, Chapt. 5*. Elsevier, Amsterdam, Netherlands, p. 167 , <https://linkinghub.elsevier.com/retrieve/pii/B9780128188705000058>
- Tsuge M., Tseng C.-Y., Lee Y.-P., 2018, *Phys. Chem. Chem. Phys.*, 20, 5344
- Wu Q. Y., Tan T. L., 2020, *J. Mol. Spect.*, 370, 111290
- Wu Q. Y., Tan T. L., 2021, *J. Mol. Spect.*, 376, 111417
- Zou L., Guillemin J.-C., Motiyenko R. A., Margulès L., 2021, *A&A*, 649, A60

SUPPORTING INFORMATION

Supplementary data are available at *MNRAS* online.

Please note: Oxford University Press is not responsible for the content or functionality of any supporting materials supplied by the authors. Any queries (other than missing material) should be directed to the corresponding author for the article.

This paper has been typeset from a $\text{\LaTeX}$ file prepared by the author.