



From CN^+ through $\text{HNC}^+/\text{HCN}^+$ to HCNH^+ at cryogenic temperatures – an isomer specific study

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Experimental determination of reaction rate coefficients for production and destruction of HCN^+ and HNC^+ in collisions with H_2 is presented. A variable temperature 22 pole rf ion trap was used to study the reactions in the temperature range of 17 – 250 K. The obtained rate coefficients for reaction of CN^+ and of HCN^+ with H_2 are close to the collisional (Langevin) value, whereas that for the reaction of HNC^+ with H_2 is quickly decreasing with increasing temperature. The product branching ratios for reaction of CN^+ with H_2 are also reported and show a notable decrease of HNC^+ product with respect to HCN^+ product with increasing temperature.



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I. INTRODUCTION

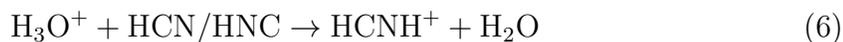
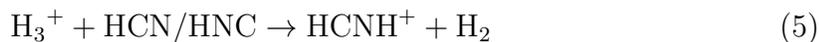
HCN and its higher energy isomer HNC (0.64 eV) have been detected in a variety of environments of interstellar medium (ISM) such as starless cores¹, diffuse², translucent³ and dense interstellar clouds⁴ and star forming regions⁵. Despite the 1.3 eV barrier for isomerization from HCN to HNC⁶, HNC abundances are often found to be comparable to that of HCN, especially in cold environments with temperatures close to 10 K⁶⁻⁸. On the other hand, the HCN/HNC abundance ratio was reported to be much greater than one in relatively warm objects such as hot cores or young stellar objects. For example, a HCN/HNC abundance ratio of 13 was observed for IRAS 16293–2422⁹, while in the vicinity of Orion-KL Nebula this ratio was approximately 80¹⁰. It has been suggested⁶ that the actual HCN/HNC abundance ratio is governed by competing processes in the given environment.

One of the main sources of HCN and HNC molecules in the interstellar medium is the dissociative recombination of HCNH^+ ions with electrons



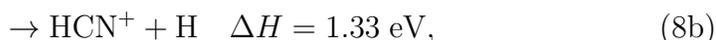
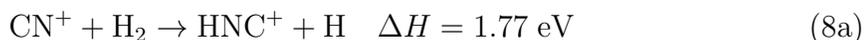
with almost the same probability of the three reaction channels¹¹. The principal processes leading to the formation of HCNH^+ ions in the interstellar medium are^{6,12,13}:





where reactions (2) and (3) are thought to be the main pathway for HCNH^+ formation in dense, cold regions such as L1544¹² while reaction (7) shall dominate in warmer environments¹³. In early times of cloud formation HCNH^+ ions are presumably produced mainly in reaction (5)¹³.

The processes leading to the production of HNC^+ and its higher energy isomer HNC^+ ions (0.94 eV) ~~are given by the physical and chemical conditions in the formation region~~⁶. In cold and dense regions, these ions are mainly produced by proton transfer reaction of H^+ with HCN/HNC or in collisions of CN^+ ions with H_2 ¹²



the enthalpies of formation are taken from ref.¹⁴. Reaction (8) was previously studied in SIFT (Selective Ion Flow Tube) experiments at 300 K by Petrie *et al.*¹⁵ and by Scott *et al.*¹⁴ who reported the value of the reaction rate coefficient to be $1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ and $1.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, respectively. In both experiments, the observed branching ratio was 0.5. In another SIFT experiment, Raksit, Schiff, and Bohme¹⁶ obtained a value of the reaction rate coefficient of $1.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ at room

temperature without distinguishing between reaction products. A slightly higher value of $1.24 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ was measured by McEwan *et al.*¹⁷ using Ion Cyclotron Resonance technique (ICR) at near thermal energies. To the best of our knowledge there are no experimental data for reaction (8) obtained at low, astrophysically relevant temperatures.

Reactions (2) and (3) were only studied by Petrie *et al.*¹⁵ at 300 K using SIFT technique. The measured reaction rate coefficients were $8.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $7.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, respectively. The scarcity of experimental data for these reactions is not surprising as it is very difficult to distinguish between the two isomer forms in experiments solely based on mass spectrometry. Chemical probing is an obvious method to enhance mass sensitive experiments to gain isomer sensitivity¹⁸.

Photon processes also play an important role in HCN/HNC (neutral/cation) abundance¹⁹. Although CN^{+20} and HCNH^{+21} have been extensively studied experimentally in submm-wave range, only a Ne matrix IR spectrum²² **XXXXXX IS THIS TRUE, CHECK! SEEMS SO! XXXXXX** and vibrational bands determined by neutral photoelectron spectroscopy^{23,24} are available for $\text{HNC}^+/\text{HCN}^+$ cations. Photon ionisation can be used to produce almost exclusively HCN^+ from HCN, contrary to e^- bombardment²⁵ (see also section II B).

The CN^- anion has been extensively studied spectroscopically in IR^{22,26} (vibration) and in radio frequency^{27,28} (rotation) and consequently detected in space²⁹. The CN^- anion does not react with H_2 and only forms a weakly bound complex at low temperatures²⁶, therefore we assume it only plays a marginal role in cyano- H_2 chemistry relevant in this context.

The present astrochemical models have difficulties to reproduce the observed HCNH^+/HCN ratios due to potentially missing important pathways or key reactions whose reaction rates are not well constrained¹³. In their recent study, Fontani, F. *et al.*¹³ conclude that in order to get the correct molecular abundances, laboratory

measurements of reactions (2), (3) and (7) are needed. This paper focuses on the experimental determination of the reaction rate coefficients for reactions (2), (3) and (8) in the temperature range of 17 – 250 K relevant for a variety of astrochemical environments.

II. METHODS

A. Experimental setup

The experimental setup is described in detail in³⁰, only a short overview will be given here. The ions are produced in the storage ion source (SIS)³¹, mass selected by passing through the first quadrupole mass filter and then refocused on the trap axis using an electrostatic bender. The 22 pole radio frequency ion trap is positioned on a RDK-101E cold head enabling operation down to 4 K. The pressure is measured by a Bayard-Alpert type ionisation gauge calibrated by a capacitance manometer CMR 375 from Pfeiffer. After a set time, the trap is opened and the ions exiting the trap are mass selected by the second quadrupole mass spectrometer and detected in a Daly type conversion detector. The trapped ions are cooled in collisions with helium gas that is introduced for few milliseconds into the trap volume at the beginning of every trapping cycle by a custom piezo valve.

To form HCN^+ and HNC^+ ions, either acetonitrile (CH_3CN) or vapors of bromium cyanide (BrCN) with water were continuously leaked into the SIS. When acetonitrile was used, a portion (about 15 %) of ions with mass 27 m/q did not react with hydrogen and oxygen molecules. We assume that this non-reacting fraction consists of C_2H_3^+ ions. The production of non reactive species was not observed when bromium cyanide was used as a precursor gas in the SIS.

In experiments focused on the reaction of CN^+ with H_2 , the use of acetonitrile

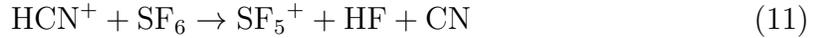
led to high fraction of ions with mass 26 m/q (almost 50 %) not reacting with H_2 nor O_2 . We tentatively identified these ions as C_2H_2^+ with reported reaction rates with H_2 at least 3 orders of magnitude lower³² than $\text{CN}^+ + \text{H}_2$ and described as “no reaction/ slow”³³ for $\text{C}_2\text{H}_2^+ + \text{O}_2$, in comparison to reaction of CN^+ with atomic O with the reaction rate of $2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ^{33,34}.

B. Fraction of HCN^+ to HNC^+ in the ion trap

We estimate the relative amount of HCN^+ to HNC^+ in the trap using isomer sensitive reaction probing. HNC^+ , the lower energy isomer by 0.94 eV, and HCN^+ have different reaction channels in ion-molecule reactions with O_2



and SF_6



with all the species in their vibrational ground states. The rate coefficients for reactions (9) and (10) were reported at 300 K as $5.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $3.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, respectively¹⁵. Reactions with SF_6 (11) and (12) were reported at 300 K as $1.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ and $1.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, respectively³⁵. All reactions are exothermic.

The number of trapped ions as a function of the storage time with a small amount of O_2 gas (ca. $5 \times 10^9 \text{ cm}^{-3}$) present in the trap volume is plotted in both panels

of Fig. 1. The primary ions with mass $27 m/q$ (HCN^+ , HNC^+ , and C_2H_3^+) were produced in the SIS from acetonitrile and then trapped and cooled (translation and vibration) using the initial He pulse. As can be seen from the lower panel of Fig. 1, the main product under these conditions are O_2^+ ions, indicating that the majority of ions with mass $27 m/q$ are HCN^+ .

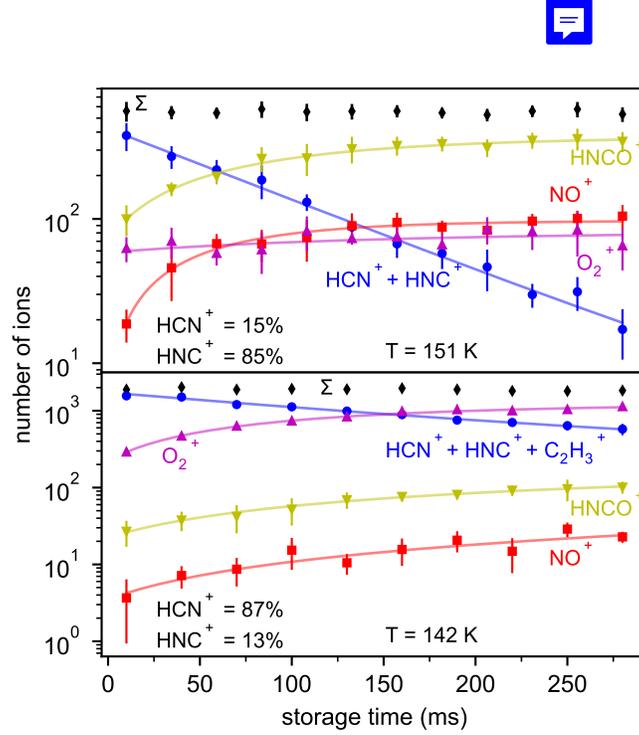
At low energies, < 0.1 eV, the collision of HCN^+ with CO or CO_2 leads to the formation of the more stable HNC^+ isomer as a result of double charge transfer in the collisional complex³⁶. We use the reaction with CO_2 in order to enhance the HNC^+ isomer in the 22-pole rf trap



The number density of CO_2 used in the experiments (order of magnitude or more than other reactants) ensures that the isomerisation reaction is dominant over reactions with O_2 for $\text{HNC}^+/\text{HCN}^+$ ratio estimation or with H_2 for reaction rates.

The upper panel of Fig. 1 illustrates the typical HNC^+ enrichment using the CO_2 technique. The dominant product in O_2 probing reaction is HNCO^+ , implying that the most prevalent isomer is HNC^+ . The actual fractions of HCN^+ and HNC^+ were calculated by solving a set of corresponding balance equations and extrapolating the numbers of ions of the given species in the trap to the time of 500 ms. Analogous results were obtained with SF_6 used as a probe gas.

It is important to note, that the addition of CO_2 directly to the ion source did not lead to a substantial change in the measured fractional populations of HCN^+ and HNC^+ in the trap. We attribute this behaviour to ions just produced by electron bombardment and still residing in the source possessing substantially more energy than few hundred meV, required for the reaction (13) to be dominant over a simple no-isomerisation collision.



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 FIG. 1: HCN⁺/HNC⁺ isomer ratio determination using O₂ probing gas. Upper panel: conditions with prevalent HNC⁺ isomer, using the CO₂ conversion reaction (13). Lower panel: conditions with prevalent higher energy HCN⁺ isomer, formed predominantly in the ion source. The sum of all the ions in the trap is denoted by Σ. The full lines are the results of fit of the data by solving set of corresponding balance equations. See reactions (9) and (10) and text.

C. Data analysis

By integrating the chemical rate equations for the ion number densities over the trap volume, balance equations describing time evolutions of the number of trapped ions n_i are obtained. As an example, for the reaction of HCN⁺ with H₂ the corresponding balance equation can be written as

$$\frac{dn_{\text{HCN}^+}}{dt} = -k_{\text{HCN}^+}^{\text{H}_2} [\text{H}_2] n_{\text{HCN}^+}, \quad (14)$$

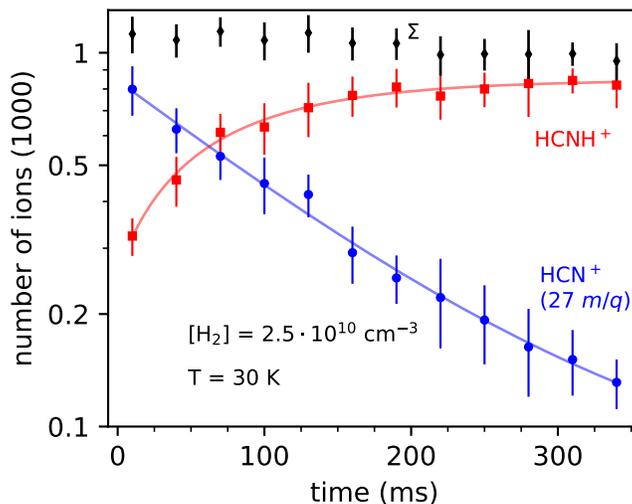
where $k_{\text{HCN}^+}^{\text{H}_2}$ is the binary rate coefficient for the reaction of HCN^+ with H_2 and $[\text{H}_2]$ is the H_2 number density. When evaluating the time dependencies of the number of ions in the trap, the quantities that are obtained by fitting the set of appropriate balance equations to the measured data are reaction rates, i. e., the reaction rate for reaction (14) is $k_{\text{HCN}^+}^{\text{H}_2}[\text{H}_2]$. The reaction rate coefficient is then determined from the slope of the dependence of the reaction rate on the number density of the corresponding reactant at the given temperature (for detailed description of the fitting procedure see ref³⁰). Throughout the text, quoted uncertainties are statistical errors of the corresponding fitting procedures. The systematic error, arising mainly from the uncertainty in pressure calibration, is estimated to be 20 %.

III. RESULTS AND DISCUSSIONS

A. $\text{HCN}^+ + \text{H}_2$

The reaction of HCN^+ with H_2 was studied in the temperature range of 17–250 K. An example of the measured time dependence of the number of ions in trap when HCN^+ was the dominant isomer is shown in Fig. 2. As the HCN^+ ions react with molecular hydrogen, HCNH^+ ions are formed as the only product of the reaction. Similar data were obtained at each temperature for several values of hydrogen number density in order to evaluate the reaction rate coefficients. The results are plotted in Fig. 3 as down facing triangles. The collisional Langevin reaction rate coefficient for this reaction is $1.54 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ using H_2 polarisability from ref³⁷. As can be seen from Fig. 3, the obtained value of the reaction rate coefficients are constant in the studied temperature range and slightly lower than the Langevin reaction rate coefficient.

The reaction of HCN^+ with H_2 was previously studied by Petrie *et al.*¹⁵ at 300 K



✓ FIG. 2: Number of ions as a function of trapping time. Typical number of HCN^+ reactants (contains traces of HNC^+ and C_2H_3^+) and HCNH^+ product ions shown at the trap temperature of $T = 30$ K. Deviation from ideal exponential decay to exponential decay with offset, caused by the non reactive C_2H_3^+ , can be seen around 300 ms. The sum of all stored ions is denoted by Σ .

using a selected-ion flow tube (SIFT) experiment. CF_4 and SF_6 were used as a probe gases to distinguish between HCN^+ and HNC^+ ions in the SIFT experiments^{15,35}. Contrary to what Petrie *et al.*³⁵ thought at that time, the ground vibrational state of HCN^+ does not react with CF_4 ³⁶ indicating that a substantial fraction of HCN^+ ions in their experiment¹⁵ was, in fact, vibrationally excited. This is the most probable explanation of almost 40 % difference between the SIFT data and the reaction rate coefficient obtained at the highest temperature of 250 K in the present study.

B. $\text{HNC}^+ + \text{H}_2$

In order to study the reaction of HNC^+ ions with H_2 , we first trapped the HCN^+ ions (with a small fraction of non reactive C_2H_3^+ ions) and converted them to HNC^+ ions inside the 22 pole trap by applying the isomerization reaction (13) with CO_2 ³⁶. The number density of used CO_2 gas was high enough to ensure that the majority of the HCN^+ ions was converted to HNC^+ before the measurement of the reaction with H_2 was performed. The only observed product of the reaction were HCNH^+ ions. For temperatures above 80 K, the CO_2 gas was added directly in to the trap, as the vapour pressure of CO_2 was sufficient (4×10^{-6} Pa at 80 K³⁸). For lower temperatures, 30 K and 70 K, the CO_2 had to be mixed with buffer gas helium and pulsed at the beginning of each trapping cycle. The charge transfer reaction between N_2^+ and CO_2 was used to check and confirm the presence of sufficient CO_2 number densities. While no depletion of CO_2 was observed down to 70 K, below this temperature CO_2 number density started to decrease reaching our detection limit between 30 – 40 K. Although the value of the reaction rate coefficient obtained for temperature of 30 K corresponds to a mixture of ions with mass 27 m/q dominated by HNC^+ , we are unable to quantify the isomeric ratio.

The measured value of the reaction rate coefficient is approximately half of the collisional Langevin rate coefficient at 250 K and increases with decreasing temperature (see Fig. 3). The 300 K SIFT value reported by Petrie *et al.*³⁵ is in very good agreement with our data.

C. $\text{CN}^+ + \text{H}_2$

The CN^+ ions were produced in the SIS from bromium cyanide with an admixture of water vapours. The majority of the trapped ions with mass 26 m/q reacted with

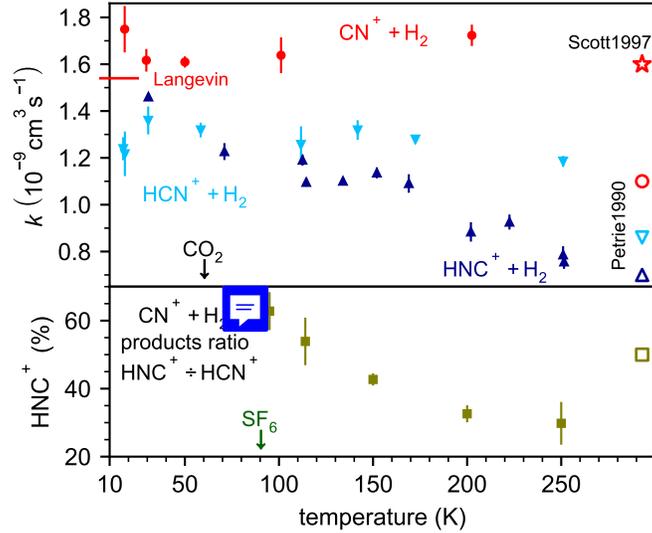


FIG. 3: Reaction rate coefficients for the reactions of CN^+ (full red circles) and HCN^+ (full cyan down facing triangles) and HNC^+ (full dark blue up facing triangles) with H_2 (top) and branching ratio for the $\text{CN}^+ + \text{H}_2$ reaction (bottom). Open symbols denote values obtained in previous studies (star¹⁴, the rest¹⁵). The corresponding value of the Langevin reaction rate coefficient is $1.54 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (for all the reactions). The down pointing arrows labelled CO_2 and SF_6 show the freeze out temperature of the respective reactants (for details see text).

hydrogen, which was leaked directly into the trap, implying that there was only a small fraction of C_2H_2^+ ions present in the trap during these experiments³⁶. The value of the reaction rate coefficient for reaction of CN^+ with H_2 was measured in the temperature range of 17 – 200 K. The results are shown in Fig. 3. The obtained value is close to the collisional Langevin reaction rate coefficient. No significant temperature dependence was observed. Our data are in excellent agreement with the study by Scott *et al.*¹⁴ performed at 300 K.

The reaction of CN^+ with H_2 results in the production of HCN^+ and HNC^+ ions.

As both these products subsequently react with hydrogen (see above), it was impossible to determine the product branching ratio with hydrogen continuously added into the trap. Instead, we added a small amount of H₂ (approximately 0.2 %) to the short helium pulse that is used to cool down ions at the beginning of each trapping period. In this way, we were able to maximize the amount of produced primary ions (HCN⁺ and HNC⁺) and to minimize the subsequent formation of secondary ions (HCNH⁺).

The actual product branching ratio was determined by utilizing different reactivity of HCN⁺ and HNC⁺ ions with SF₆, which was added directly **in to** the trap. An example of the measured number of ions in the trap as a function of storage time is shown in Fig. 4. SF₅⁺ is formed in reactions of CN⁺ as well as HCN⁺ and vibrationally excited HNC⁺ with SF₆, i. e., this channel is not suitable for product isomer probing. Solely HNC⁺ ions in the ground state reacting with SF₆ do form HNCF⁺. Therefore, the HNC⁺ fraction was determined from the increase of the number of HNCF⁺ ions compared to the decrease of the ions of mass 27 *m/q*. The measured HNC⁺/HCN⁺ product branching ratios are shown in lower panel of Fig. 3. At 250 K, almost 70 % of all ions produced in reaction of CN⁺ with H₂ are HCN⁺. As the temperature decreases, reaction (8) results in larger fraction of produced HNC⁺ ions and below 100 K the HNC⁺ channel of reaction (8) accounts for more than 60 % of total produced ions.

This is in disagreement with results of Petrie *et al.*³⁵ who observed the same probability of both channels of reaction (8) at 300 K. As discussed above in relation with the study of the reaction of HCN⁺ with H₂, it is possible that the CN⁺ ions in the study by Petrie *et al.*³⁵ were vibrationally excited. While we are absolutely certain that in our experiment the primary CN⁺ ions are in their vibrational ground state, we can not rule out that some of the HCN⁺ and HNC⁺ ions produced inside the trap (reaction (8)) possess some vibrational excitation. As reaction (8b) is exothermic

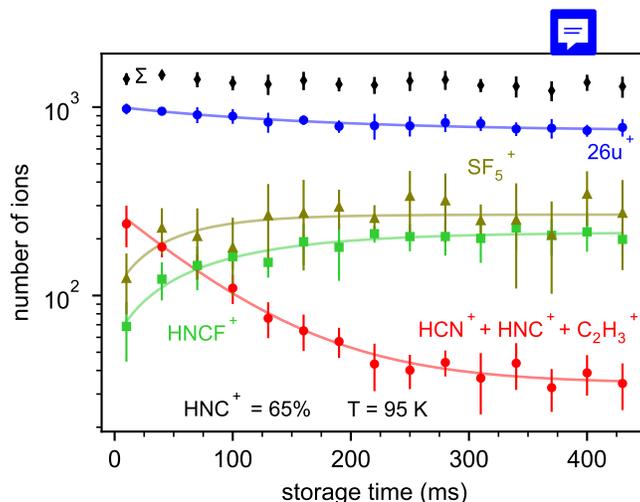


FIG. 4: Determination of the ratio of the products of the $\text{CN}^+ + \text{H}_2$ reaction. SF_6 was used as a reaction product isomer probing gas. The SF_5^+ ions are products of the reaction of either CN^+ or HCN^+ with SF_6 . Only ground state HNC^+ produces HNCF^+ in reaction with SF_6 . The HNC^+ fraction is determined from the increase of number of HNCF^+ ions compared to the decrease of number of ions with mass $27 m/q$. The primary mass $26 m/q$ corresponds to an undetermined ratio of CN^+ and C_2H_2^+ ; the latter is non reactive. The ion signal for SF_5^+ is multiplied by a factor of 5.5 to account for the sensitivity of the detection system.

by 1.33 eV^{14} , HNC^+ ions can have enough internal energy available to form SF_5^+ ions in reaction with SF_6 ³⁶ and thus influence our data analysis to overestimate the HCN^+ fraction of produced ions. Therefore, our $\text{HNC}^+/\text{HCN}^+$ product branching ratios shall be interpreted as lower limit; the ratio may be higher, but not lower than reported.

D. $\text{CN}^+ + \text{O}_2$

The reaction rate coefficient for reaction



was determined between 100 and 230 K. Acetonitrile (all temperatures) and bromium cyanide with admixture of water vapours (152 K) was used as a precursor to form CN^+ ions in the SIS (see Fig. 5.) The major product of the reaction was O_2^+ accounting for more than 80 % of the produced ions, followed by NCO^+ (less than 20 % of product ions) and NO^+ (few percent of produced ions). NCO^+ ions reacted slowly with O_2 , complicating the determination of the product branching ratios. For comparison, Raksit, Schiff, and Bohme¹⁶ reported the product branching ratios for reaction (15) as 0.6:0.2:0.2 at room temperature.

The measured data shows a very steep increase with decreasing temperature and is in a good agreement with the previous 300 K SIFT experimental value¹⁶. Although the corresponding collisional Langevin reaction rate coefficient $k_L = 7.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ is of the same order of magnitude as the measurement, the comparison is only made for reference as the measured dependence implies a barrier in the reaction path of overall exothermic reaction.

E. Attempt at electronic spectroscopy of HNC^+

We attempted to perform electronic spectroscopy of HNC^+ cation in photon energy range 1.6 – 2.5 eV using laser induced charge transfer (LICT) action scheme of ions stored in the 22 pole trap at ca. 150 K to avoid any kind of neutral freeze out.

The range has been selected for $X^+ \ ^2\Sigma^+ \rightarrow A^+ \ ^2\Pi$ HNC^+ transition predicted by previous computational results around 2 eV²⁴. LICT of HNC^+ to Xe ($\Delta \sim 0.1$ eV) as well as to CO_2 ($\Delta \sim 1.6$ eV, note that CO_2 is more suitable for LICT studies of higher energy isomer HCN^+)³⁶ has been attempted using a supercontinuum laser³⁰ with HNC^+ ions produced as described in section III B. Unfortunately no visible signal could be recorded. While the **afore mentioned** LICT schemes for IR vibrational and VIS electronic studies of HNC^+ should be straightforward and very effective, the lack of experimental spectroscopic data for $\text{HCN}^+/\text{HNC}^+$ in gas phase remains remarkable.

F. Comparison to other processes involved in HCNH^+ formation in ISM

A comparison of the reaction rate coefficients obtained in present study with those measured for other HCNH^+ formation processes by Clary, Smith, and Adams³⁹ is shown in Fig. 5. In cold, dense regions of the interstellar medium the most important gas phase processes for the formation of HCN^+ and HNC^+ ions are considered to be¹² reaction (8) and the charge transfer reaction



Clary, Smith, and Adams³⁹ studied reaction (16) for HCN reactant and reported values of the reaction rate coefficient close to $1 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ and practically independent on temperature between 205 and 540 K. The calculated exothermicity of reaction (16) is $8 \pm 10 \text{ meV}$ ³⁹, therefore reaction (16) could be slightly endothermic and the value of its reaction rate coefficient at temperatures close to 10 K much lower than that reported by Clary, Smith, and Adams³⁹ at higher temperatures. In that case, reaction (8) proceeding with almost Langevin reaction rate coefficient, would

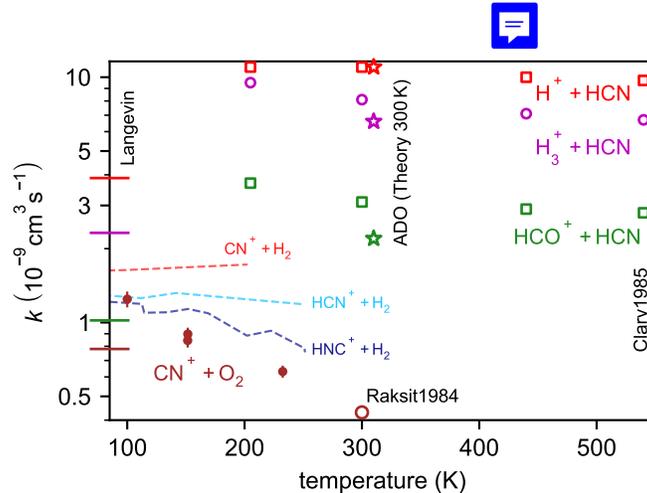


FIG. 5: Rate coefficients of **ion molecule** reactions leading to HCNH^+ as a function of temperature. Data for reaction of CN^+ , HCN^+ , and HNC^+ with H_2 from Fig. 3 (dashed lines). Previous experimental data for H^+ , H_3^+ , and HCO^+ with HCN (red, magenta, green open symbols)³⁹, including the theoretical **ADO** approximation (stars)³⁹. Reaction rate of $\text{CN}^+ + \text{O}_2$ (brown), with previous room temperature SIFT value (brown open circle)¹⁶ shown for reference. Langevin reaction rates are illustrated by horizontal lines on the left abscissa.

be the dominant process for HCNH^+ formation in such environments.

The ~~astrochemical~~ databases such as KIDA⁴⁰ contain usually reaction rate coefficients for reactions (2), (3) and (8) that were measured by Petrie *et al.*¹⁵ at 300 K with unknown fraction of vibrationally excited ions. According to the present data obtained with vibrationally cold ions at low temperatures, the actual values of reaction rate coefficients for reactions (2) and (8) are higher by a factor of up to 1.6. In case of low temperature HCNH^+ formation in reaction of HNC^+ with H_2 (3) the ratio between our value of reaction rate coefficient and that in KIDA entry is almost two times. As a result, the astrochemical models employing these database values are probably underestimating the $\text{HCN}^+/\text{HNC}^+$ and HCNH^+ formation in cold, dense



regions of interstellar medium.

The branching ratio for reaction (8) is 1:1 in KIDA database in accordance with 300 K value reported by Petrie *et al.*¹⁵. Although our data show that at 250 K almost 70 % of products of reaction (8) are HCN⁺ ions, the branching ratio is close to that in KIDA database around 100 K. Unfortunately, we were not able to measure the branching ratio of reaction (8) to lower temperatures due to employed chemical probing scheme. Given the observed temperature dependence, it is possible, that in regions of cold interstellar gas, where reaction (8) is a key formation process for HCN⁺ and HNC⁺ ions, the actual branching ratio strongly favours HNC⁺ production.

IV. CONCLUSION

The formation and destruction of HCN^+ and HNC^+ isomers in reactions with H_2 were studied in the temperature range of 17 – 250 K. The values of the reaction rate coefficients for reactions of CN^+ and HCN^+ with H_2 are constant in the studied temperature range and close to the collisional Langevin reaction rate coefficient. The reaction of CN^+ with H_2 produces predominantly HCN^+ at 250 K, but below 100 K, HNC^+ is the more favoured. The obtained values of the reaction rate coefficient for reaction of HNC^+ with H_2 decrease with increasing temperature. We believe that our results will help to improve models of cyanide chemistry in the interstellar medium.

The isomer specific results in this work were achieved solely using chemical probing. This technique is fully dependent on availability of chemicals with the right energy levels with respect to the isomers being studied. Even then, the process is rather tedious, since several reactants have to be used in sequence (e. g. isomerisation/ reactivity/ probing) with tight control of the real number density inside the trap, especially while lowering the temperature towards the neutral gas freeze out. While we have demonstrated that rf multipole ion traps are a suitable tool for isomer specific studies, the application of novel techniques and schemes based on direct discrimination of ions with different kinetic energy (e. g. the reaction of CN^+ with H_2 releases two equal m/q products with two distinctive total energies), as described in Jusko, Jiménez-Redondo, and Caselli³⁰, or indirectly, based on the transfer of the internal excitation to translation energy in a collision with a neutral, as described in the “leak out” method⁴¹, shall be developed.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Paola Caselli: Conceptualization, Funding acquisition, Investigation, Writing – review & editing. Petr Dohnal: Conceptualization, Funding acquisition, Investigation, Writing – original draft. Miguel Jiménez-Redondo: Conceptualization, Data curation, Investigation, Writing – review & editing. Pavol Jusko: Conceptualization, Data curation, Investigation, Visualization, Writing – original draft.

DATA AVAILABILITY

The data that support the findings of this study are openly available at <http://doi.org/10.5281/zenodo.584444>.
During the review process the archive can be accessed here: XXX

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