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ABSTRACT

The experimental determination of the reaction rate coefficients for production and destruction of HCN^+ and HNC^+ in collision with H_2 is presented. A variable-temperature, 22-pole radio frequency ion trap was used to study the reactions in the temperature range 17–250 K. The obtained rate coefficients for the reaction of CN^+ and 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 the reaction of CN^+ with H_2 are also reported and show a notable decrease of the HNC^+ product with respect to the HCN^+ product with increasing temperature. These measurements have consequences for current astrochemical models of cyanide chemistry, in particular, for the HCNH^+ cation.

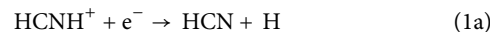
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I. INTRODUCTION

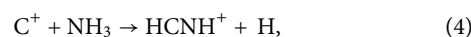
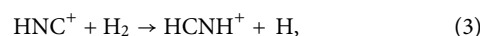
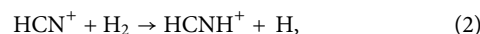
HCN and its higher energy isomer HNC (0.64 eV) are presumably the two simplest isomers in chemistry. On earth, at 300 K, the HCN isomer is populated almost exclusively. Both isomers have been detected in a variety of environments of the interstellar medium (ISM) such as starless cores,¹ diffuse,² translucent,³ and dense interstellar clouds,⁴ and star⁵ and planet^{6–8} forming regions. Despite the 1.3 eV barrier for isomerization from HCN to HNC,⁹ HNC abundances are often found to be comparable to that of HCN, especially in cold environments with temperatures close to 10 K.^{9–11} On the other hand, the HCN/HNC abundance ratio was reported to be much greater than the 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 16293–2422,¹² while in the vicinity of the Orion-KL nebula this ratio was ~80.¹³ It has been suggested⁹ that the actual HCN/HNC abundance ratio is governed by competing processes in the given environment. However, as noted by Hernández Vera *et al.*,¹⁴ special care needs to be taken in interpreting the observations, as the rate coefficients for HCN and HNC differ

significantly, especially when the collision partner is para- H_2 —the dominant form of H_2 in cold gas (e.g., Brünken *et al.*¹⁵).

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



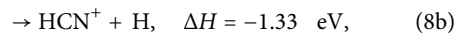
with almost the same probability for the three reaction channels.¹⁶ The principal processes leading to the formation of HCNH^+ ions in molecular clouds are^{9,17,18}





where reactions (2) and (3) are thought to be the main pathway for HCNH^+ formation in dense, cold regions such as L1544,¹⁷ while reaction (7) shall dominate in warmer environments.¹⁸ In early times of cloud formation, HCNH^+ ions are presumably produced mainly in reaction (5).¹⁸

The processes leading to the production of HNC^+ and its higher energy isomer HCN^+ ions (0.94 eV) depend on the physical and chemical conditions of the molecular cloud. In cold and dense regions, these ions are mainly produced by the proton transfer reaction of H^+ with HCN/HNC or in collisions of CN^+ ions with H_2 .¹⁷



with the enthalpies of formation, ΔH , taken from Ref. 19. Reaction (8) was previously studied in SIFT (Selective Ion Flow Tube) experiments at 300 K by Petrie *et al.*²⁰ and by Scott *et al.*,¹⁹ who reported the value of the reaction rate coefficient to be 1.1×10^{-9} and $1.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, respectively. In both experiments, the observed branching ratio was 0.5 (i.e., the two reaction channels were equally probable). In another SIFT experiment, Raksit, Schiff, and Bohme²¹ 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.*²² using the 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.*²⁰ at 300 K using the SIFT technique. The measured reaction rate coefficients were 8.6×10^{-10} 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 sensitivity.²³

Photon processes also play an important role in the HCN/HNC (neutral/cation) abundance.²⁴ Although CN^{+25} and HCNH^{+26} have been extensively studied experimentally in the mm-wave range, only a Ne matrix IR spectrum²⁷ and the vibrational bands determined by neutral photoelectron spectroscopy^{28–30} are available for $\text{HNC}^+/\text{HCN}^+$ cations. Photon ionization can be used to produce, almost exclusively, HCN^+ from HCN , contrary to e^- bombardment³¹ (see also Sec. II B).

The CN^- anion has been extensively studied spectroscopically in the IR^{27,32} (vibration) and mm-wave range^{33,34} (rotation) and consequently detected in space.³⁵ The CN^- anion does not react with H_2 and only forms a weakly bound complex at low temperatures;³² therefore, we assume that it only plays a marginal role in the cyano- H_2 chemistry relevant in this context.

Due to the simplicity of the HCN/HNC isomerization process and the small size of the system, it is extensively studied theoretically, often employing very high levels of theory or to benchmark new methods.^{36–38}

The present astrochemical models have difficulties in reproducing the observed HCNH^+/HCN ratios due to the potential absence of important pathways or key reactions whose reaction rates are not well constrained.¹⁸ In their recent study, Fontani *et al.*¹⁸ concluded 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 17–250 K, relevant for a variety of astrochemical environments.

II. METHODS

A. Experimental setup

The experimental setup is described in detail in Ref. 39; only a short overview will be given here. The ions are produced in the storage ion source (SIS),⁴⁰ 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 cold head (RDK-101E, Sumitomo), enabling operation down to 4 K. The pressure is measured by a Bayard–Alpert type ionization gauge, calibrated by a capacitance manometer, CMR 375, from Pfeiffer. After a set storage 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 a few milliseconds into the trap volume at the beginning of every trapping cycle by a custom piezo valve. This measurement sequence is repeated, usually at 1 Hz repetition rate, until an adequate signal for the set experimental condition is acquired.

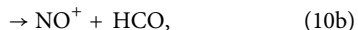
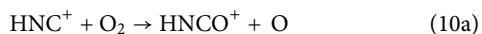
To form HCN^+ and HNC^+ ions, either acetonitrile (CH_3CN) or vapors of bromium cyanide (BrCN) with water, producing HCN , were continuously leaked into the SIS. When acetonitrile was used, a portion (about 15%) of ions with mass $27m/z$ did not react with hydrogen and oxygen molecules. Here, and in the following text, m/z denotes the mass-to-charge ratio. We assume that this non-reacting fraction consists of C_2H_3^+ ions. The production of a 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 a high fraction of ions with mass $26m/z$ (almost 50%) not reacting with H_2 or O_2 . We tentatively identified these ions as C_2H_2^+ , with reported reaction rates with H_2 at least 3 orders of magnitude lower⁴¹ than that for $\text{CN}^+ + \text{H}_2$ and described as “no reaction/slow”⁴² for $\text{C}_2\text{H}_2^+ + \text{O}_2$, in comparison to the reaction of CN^+ with atomic O with the reaction rate of $2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.^{42,43}

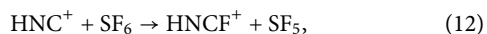
B. Ratio of HCN^+ to HNC^+ in the ion trap

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 SF₆:



with all the species in their vibrational ground states. The rate coefficients for reactions (9) and (10) were reported at 300 K as 5.0×10^{-10} and $3.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, respectively.²⁰ Reactions with SF₆ (11) and (12) were reported at 300 K as 1.3×10^{-9} and $1.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, respectively.⁴⁴ All those reactions are exothermic.

The number of trapped ions as a function of the storage time with a small amount of O₂ gas ($\sim 5 \times 10^9 \text{ cm}^{-3}$) present in the trap volume is plotted in both panels of Fig. 1. The primary ions with mass $27m/z$ (HCN⁺, HNC⁺, and C₂H₃⁺) 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 upper panel of Fig. 1, the main products under these conditions are O₂⁺ ions, indicating that the majority of ions with mass $27m/z$ are HCN⁺.

At low energies, <0.1 eV, the collision of HCN⁺ with CO or CO₂ leads to the formation of the more stable HNC⁺ isomer as a result of double charge transfer in the collisional complex.⁴⁵ CO₂ is added into the trap volume to enhance the fraction of the HNC⁺ isomer inside the trap using the catalytic reaction

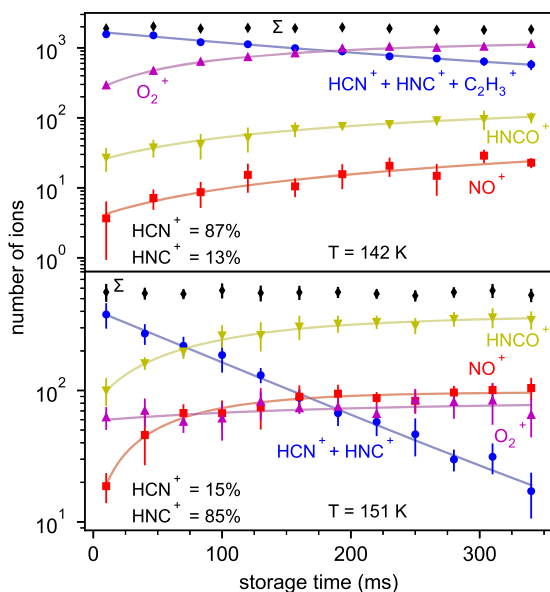
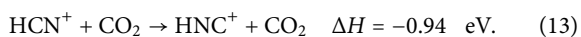


FIG. 1. HCN⁺/HNC⁺ isomer ratio determination using O₂ probing gas. Upper panel: conditions with prevalent higher energy HCN⁺ isomer, formed predominantly in the ion source. Lower panel: conditions with prevalent HNC⁺ isomer, using the CO₂ conversion reaction (13). The sum of all the ions in the trap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

The number density of CO₂ used in the experiments (order of magnitude or more than other reactants) ensures that the isomerization reaction is dominant over reactions with O₂ for HNC⁺/HCN⁺ ratio estimation or with H₂ for reaction rates.

The lower panel of Fig. 1 illustrates the typical HNC⁺ enrichment using the CO₂ technique. The dominant product in the O₂ probing reaction is HNCO⁺, implying that the most prevalent isomer is HCN⁺. The actual fractions of HCN⁺ and HNC⁺ were calculated by solving a set of corresponding balance equations (see Sec. II C) and extrapolating the numbers of ions of the given species in the trap to the time of 500 ms. Analogous results were obtained with SF₆ used as a probe gas.

It is important to note that the addition of CO₂ 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 behavior to the relatively high energy of ions in the source. Ions just produced by electron bombardment are substantially more energetic than few hundred meV, which is required for reaction (13) to be dominant over a simple no-isomerization collision.

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 H₂, and [H₂] is the H₂ 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 a detailed description of the fitting procedure, see Ref. 39). 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%.³⁹

III. RESULTS AND DISCUSSIONS

A. HCN⁺ + H₂

The reaction of HCN⁺ with H₂ was studied in the temperature range 17–250 K. An example of the measured time dependence of the number of ions in the 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 (see Fig. 3 for a typical reaction rate plot as a function of number density). The results are plotted in Fig. 4 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 H₂ polarizability from Ref. 46. As can be

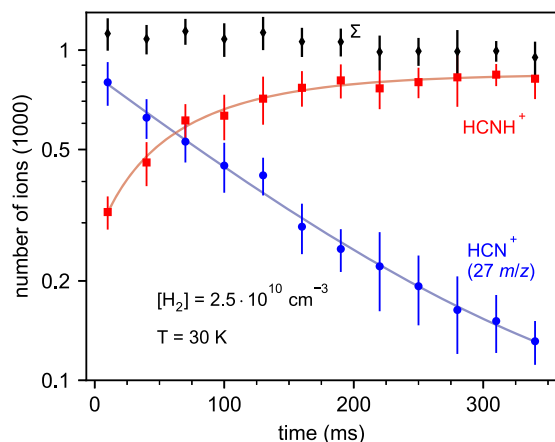


FIG. 2. Number of ions as a function of trapping time. Typical number of HCN^+ reactants (contains traces of HNC^+ and C_2H_3^+) and HCNH^+ product ions, shown at the trap temperature of $T = 30$ K. Deviation from the ideal exponential decay to exponential decay with offset, caused by the non-reactive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

seen from Fig. 4, 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.*²⁰ at 300 K using a selected-ion flow tube (SIFT) experiment. CF_4 and SF_6 were both used as probe gases to distinguish between HCN^+ and HNC^+ ions in the SIFT experiments.^{20,44} Contrary to what Petrie *et al.*⁴⁴ thought at that time, the ground vibrational state of HCN^+ does not react with CF_4 ⁴⁵ indicating that a substantial fraction of HCN^+ ions in their experiment²⁰ were, in fact, vibrationally excited. This could be a possible explanation for the almost 40% difference between the SIFT data and the reaction rate coefficient obtained at the highest temperature of 250 K in the present study.

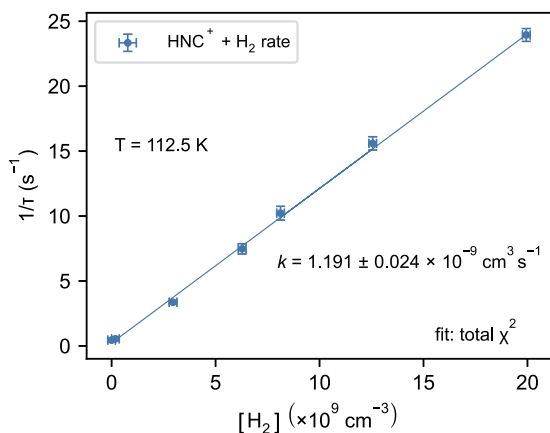


FIG. 3. Typical rate of the reaction as a function of the H_2 number density in the trap, here depicted for reaction (3) at the trap temperature of $T = 112.5$ K. The slope corresponds to the rate coefficient k (see text and Ref. 39).

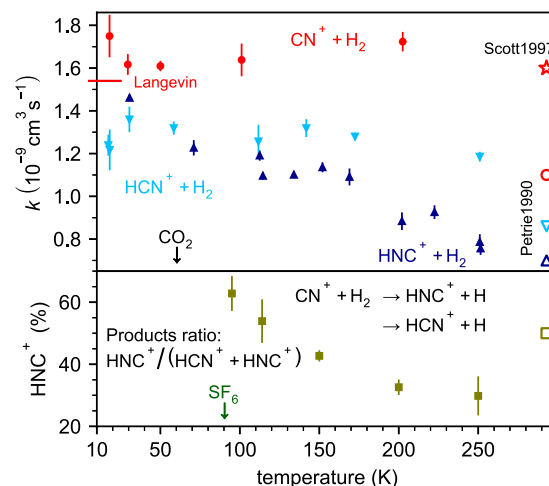


FIG. 4. Reaction rate coefficients for the reactions of CN^+ (full red circles), HCN^+ (full cyan, down-facing triangles), and HNC^+ (full dark blue, up-facing triangles) with H_2 (top) and branching ratio for the $\text{CN}^+ + \text{H}_2$ reaction (bottom). Open symbols denote values obtained in previous studies (star,¹⁹ the rest²⁰). 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 labeled CO_2 and SF_6 show the freeze-out temperature of the respective reactants (for details see text).

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 .⁴⁵ The CO_2 number density was high enough to ensure that the majority of the HCN^+ ions were converted to HNC^+ before the measurement of the reaction with H_2 was performed. The only observed product of the reaction was HCNH^+ ions. For temperatures above 80 K, the CO_2 gas was added directly into the trap, as the vapor pressure of CO_2 was sufficient (4×10^{-6} Pa at 80 K⁴⁷). For lower temperatures, 30 and 70 K, the CO_2 had to be mixed with the helium buffer gas 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, the CO_2 number density started to decrease, reaching our detection limit between 30 and 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/z 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. 4). The 300 K SIFT value reported by Petrie *et al.*⁴⁴ 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 vapors. The majority of the trapped ions with mass 26 m/z reacted with 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 experiments.⁴⁵ The value of the reaction rate coefficient for reaction of CN^+ with H_2 was measured in the temperature range 17–200 K. The results are shown in Fig. 4. 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.*¹⁹ 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 H_2 (~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 minimize the subsequent formation of secondary ions ($HCNH^+$).

The actual product branching ratio was determined by utilizing the different reactivity of HCN^+ and HNC^+ ions with SF_6 , which was added directly into the trap. An example of the measured number of ions in the trap as a function of storage time is shown in Fig. 5. SF_5^+ is formed in reactions of CN^+ as well as HCN^+ and vibrationally excited HNC^+ with SF_6 , i.e., this channel is not suitable for product isomer probing. Solely, HNC^+ ions in the ground state reacting with SF_6 do form $HCNF^+$. Therefore, the HNC^+ fraction was determined from the increase of the number of $HCNF^+$ ions compared to the decrease of the ions of mass 27 m/z . The measured HNC^+/HCN^+ product branching ratios are shown in lower panel of Fig. 4. At 250 K, almost 70% of all ions produced in the reaction of CN^+ with H_2 are HCN^+ . As the temperature decreases, reaction (8) results in a larger fraction of produced HNC^+ ions, and below 100 K, the HNC^+ channel of reaction (8) accounts for more than 60% of the total produced ions.

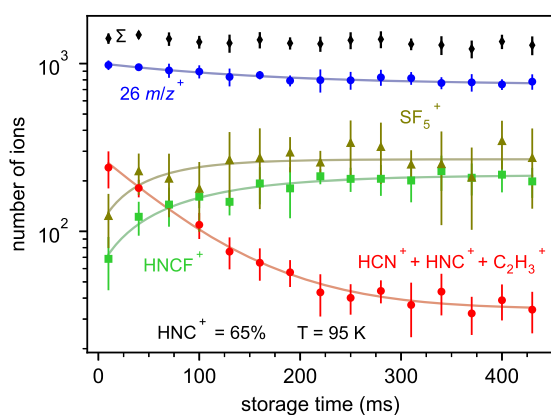


FIG. 5. Determination of the ratio of the products of the $CN^+ + H_2$ reaction. SF_6 was used as a reaction product isomer probing gas. The SF_5^+ ions are products of the reaction of either CN^+ or HCN^+ with SF_6 . Only ground state HNC^+ produces $HCNF^+$ in reaction with SF_6 . The HNC^+ fraction is determined from the increase of the number of $HCNF^+$ ions compared to the decrease of the number of ions with mass 27 m/z . The primary mass 26 m/z 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.

This is in disagreement with the results of Petrie *et al.*,⁴⁴ who observed the same probability of both channels of reaction (8) at 300 K. As discussed above in relation to the study of the reaction of HCN^+ with H_2 , it is possible that the CN^+ ions in the study by Petrie *et al.*⁴⁴ were vibrationally excited. While we are absolutely certain that in our experiment the primary CN^+ ions are in their vibrational ground state, we cannot rule out that some of the HCN^+ and HNC^+ ions produced inside the trap [reaction (8)] possess some vibrational excitation. As reaction (8a) is exothermic by 2.28 eV,¹⁹ HNC^+ ions can have enough internal energy available to form SF_5^+ ions in reaction with SF_6 ⁴⁵ and, thus, influence our data analysis, to overestimate the HCN^+ fraction of produced ions. Therefore, our HNC^+/HCN^+ product branching ratios shall be interpreted as the lower limit; the ratio may be higher, but not lower than that reported.

D. $CN^+ + O_2$

The reaction rate coefficient for the reaction



was determined between 100 and 230 K. Acetonitrile (all temperatures) and bromium cyanide with admixture of water vapors (152 K) were used as precursors to form CN^+ ions in the SIS (see Fig. 6). The major product of the reaction is 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 Bohme²¹ reported the product branching ratios for reaction (15) as 0.6:0.2:0.2 at room temperature.

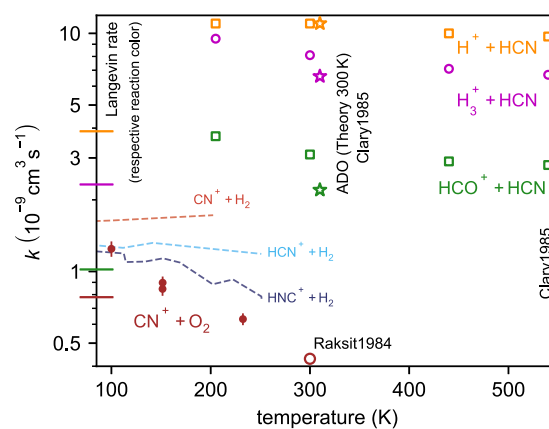


FIG. 6. Rate coefficients of ion–molecule reactions, leading to $HCNH^+$, as a function of temperature. Data for reaction of CN^+ , HCN^+ , and HNC^+ with H_2 from Fig. 4 (dashed lines). Previous experimental data for H^+ , H_3^+ , and HCO^+ with HCN (orange, magenta, and green open symbols),⁴⁸ including the theoretical average dipole orientation (ADO) approximation (stars).⁴⁸ Reaction rate of $CN^+ + O_2$ (brown), with previous room temperature SIFT value (brown open circle)²¹ shown for reference. Langevin reaction rates are illustrated by horizontal lines on the left abscissa.

The measured rate coefficient shows a very steep increase with decreasing temperature and is in good agreement with the previous 300 K SIFT experimental value.²¹ 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 experimentally determined rate coefficient, the comparison is only made for reference, as the measured dependence implies a barrier in the reaction path of the overall exothermic reaction.

E. Attempt at electronic spectroscopy of HNC⁺

We attempted to perform electronic spectroscopy of HNC⁺ cation in the photon energy range 1.6–2.5 eV using a laser-induced charge transfer (LICT) action scheme of ions stored in the 22-pole trap at ~150 K to avoid any kind of neutral freeze out. The range has been selected for the X²Σ⁺ → A²Π HNC⁺ transition, predicted by previous computational results around 2 eV.³⁰ LICT of HNC⁺ to Xe (Δ ~ 0.1 eV), as well as to CO₂ (Δ ~ 1.6 eV, note that CO₂ is more suitable for LICT studies of the higher energy isomer HCN⁺),⁴⁵ has been attempted using a supercontinuum laser,³⁹ with HNC⁺ ions produced as described in Sec. III B. Unfortunately, no action spectroscopic signal could be recorded. While the aforementioned LICT schemes for IR vibrational and VIS electronic studies of HNC⁺ should be straightforward and very effective, the lack of experimental spectroscopic data for HCN⁺/HNC⁺ in gas phase remains remarkable.

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

A comparison of the reaction rate coefficients obtained in the present study with those measured for other HCNH⁺ formation processes by Clary, Smith, and Adams⁴⁸ is shown in Fig. 6. 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 be¹⁷ reaction (8) and the charge transfer reaction



Clary, Smith, and Adams⁴⁸ studied reaction (16) for the HCN reactant and reported values of the reaction rate coefficient close to $1 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$, practically independent of temperature between 205 and 540 K. The calculated exothermicity of reaction (16) is $8 \pm 10 \text{ meV}$;⁴⁸ 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 Adams⁴⁸ at higher temperatures. In that case, reaction (8) proceeding with almost the Langevin reaction rate coefficient, would be the dominant process for HCN⁺ formation in such environments.

Astrochemical databases such as KIDA⁴⁹ usually contain the reaction rate coefficients for reactions (2), (3), and (8) that were measured by Petrie *et al.*²⁰ at 300 K with an 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 the case of low temperature HCNH⁺ formation in the reaction of HNC⁺ with H₂ (3), the ratio between our value of the reaction rate coefficient and that in the KIDA entry is almost two. As a result, the astrochemical models employing these database

TABLE I. Parameterized reaction rate coefficients using Arrhenius–Kooij formula⁴⁹ $k(T) = A(T/300)^B \exp(-C/T)$.

Reaction	T_{range} (K)	A^a	B	C^b
CN ⁺ + H ₂ (8)	10–300	16.67 ± 0.29		
CN ⁺ + O ₂ (15)	95–300	4.72 ± 0.26	−0.889 ± 0.075	
HCN ⁺ + H ₂ (2)	10–300	12.7 ± 0.02		
HNC ⁺ + H ₂ (3)	10–90	12.7 ± 0.02 ^c		
	90–300	9.52 ± 0.69	−1.02 ± 0.27	88 ± 34

^aIn $10^{-10} \text{ cm}^3 \text{ s}^{-1}$.

^bIn K.

^cSame as the reaction HCN⁺ + H₂; The statistical errors of the least square fit are reported.

values are probably underestimating the HCN⁺/HNC⁺ and HCNH⁺ formation in cold, dense regions of the interstellar medium.

The branching ratio for reaction (8) is 1:1 in the KIDA database, in accordance with the 300 K value reported by Petrie *et al.*²⁰ 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 the KIDA database around 100 K. Unfortunately, we were not able to measure the branching ratio of reaction (8) to lower temperatures due to the 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 favors HNC⁺ production.

G. Parameterized reaction rates coefficients

The temperature-dependent reaction rate coefficients of reactions (2), (3), (8), and (15) measured in this work have been parameterized using the Arrhenius–Kooij formula as defined in Eq. (1) in Ref. 49. The results of the least square fit, together with the temperature range where the fit is valid, are reported in Table I. The CN⁺ + O₂ room temperature measurement²¹ has been included in the fit. Detailed procedures are available in the dataset associated with this work (see Data Availability).

IV. CONCLUSION

The formation and destruction of HCN⁺ and HNC⁺ isomers in reactions with H₂ were studied in the temperature range 17–250 K. The values of the reaction rate coefficients for reactions of CN⁺ and HCN⁺ with H₂ are constant in the studied temperature range and close to the collisional Langevin reaction rate coefficient. The reaction of CN⁺ with H₂ produces predominantly HCN⁺ at 250 K, but below 100 K, HNC⁺ is favored. The obtained values of the reaction rate coefficient for the reaction of HNC⁺ with H₂ decrease with increasing temperature. As current astrophysical databases such as KIDA⁴⁹ contain rate coefficients for these key reactions that were obtained at 300 K, in some cases with vibrationally excited ions, 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 the 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. isomerization/reactivity/probing), with tight control of the real number density inside the trap, especially while lowering the temperature toward the neutral gas freeze out. While we have demonstrated that multipole radiofrequency 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 energies (e.g. the reaction of CN^+ with H_2 releases two equal m/z products with two distinctive total energies), as described in Jusko, Jiménez-Redondo, and Caselli,³⁹ or, indirectly, based on the transfer of the internal excitation to translation energy in collision with a neutral, as described in the “leak out” method,⁵⁰ shall be developed.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

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

DATA AVAILABILITY

The data that support the findings of this study are openly available in Zenodo at <http://doi.org/10.5281/zenodo.7704359>.

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