

FACULTY  
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HABILITATION THESIS

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ASTROPHYSICALLY RELEVANT REACTIONS OF IONS WITH  
MOLECULAR AND ATOMIC HYDROGEN

Field: Physics – Plasma Physics

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## PREFACE

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This thesis summarizes the results of my research carried out in the years 2012—2021 at the Faculty of Mathematics and Physics of the Charles University and at the Institute for Ion Physics and Applied Physics of the University of Innsbruck. The thesis takes the form of a commented collection of articles and the main body of my work is documented in detail in the publications listed at page 55 and in the attached core publications.

## ACKNOWLEDGMENTS

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I am grateful to all my collaborators at the Department of Surface and Plasma Science, Faculty of Mathematics and Physics of Charles University and Their contributions to the presented research were essential.

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## INTRODUCTION

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Since the early days of astronomical spectroscopy, it has been known that the interstellar medium (ISM) is populated with neutral or ionized molecules (see, e. g., Refs. [1, 2]). The spectroscopy of the interstellar molecules then proved to be an immensely useful tool for obtaining detailed information about the conditions in the ISM, as the velocities, kinetic temperatures, internal temperatures, or number densities of observed molecules can be readily obtained from the observed line shapes and intensities *if* the molecular transition energies and strengths are known. Since, even for diatomic molecules, the ab-initio calculated spectra generally do not achieve the required accuracy, the laboratory spectroscopy in combination with quantum theory became the primary tools for interpretation and identification of the observed spectra.

In order to gain a better understanding and to extract more information from the observed number densities of various species, astronomers then turned to chemical kinetic modeling of the interstellar medium (see, e. g., Refs. [3–6]). The kinetic models are built on the basis of known reaction rate coefficients and these can again (with very few exceptions) only be reliably determined in experimental studies. This demand for measurements of reaction rate coefficients then motivated a rapid growth of the field of laboratory astrochemistry.

Until now, approximately 250 different species (neutral or ionic) have been identified in the ISM, with more than 30 new molecules discovered just in the last year [7]. The molecules are ranging from simple diatomics through numerous hydrides and organic molecules up to polycyclic aromatic hydrocarbons and fullerenes (see, e. g., Refs. [8–10] for a few examples).

The complex molecules are most frequently found in the diffuse or dense interstellar clouds. The typical temperatures in these environments are between 10 and 100 K (see, e. g., Ref. [11] for a review) and at such low temperatures, gas-phase reactions among neutral molecules tend to be very slow due to their activation energies. The chemistry is therefore driven mainly by ion-neutral reactions, where the ion-induced dipole interaction often leads to the absence of reaction barriers, or by reactions on the surface of dust (or ice) grains. The focus of the presented work is solely in the area of gas-phase reactions.

There are multiple tightly connected motivations to do chemical modeling of the ISM. The first one is, to explain how specific molecules can be formed in the ISM, which involves building a network of chem-

ical reactions that describe the production and destruction mechanisms of the studied species. This process often identifies new reactions and species that should be added to the model. Once the process of formation is understood, the observed abundances can be used in connection with astrochemical models to deduce information about the conditions in the observed cloud. I. e., the number densities or other parameters of the observed species can be used as proxies for quantities, that are not directly observable.

For example observation of the number density of selected cations can reveal information about the local ionization rate [12], or about the fraction of molecular hydrogen [13]. Much more information can be derived if one considers also the isotopic composition and quantum states of the observed molecules. The isotopic composition of molecules can encode information about the conditions during the molecule formation (see, e. g., Refs. [14, 15]), or, more specifically, it can be used as a proxy for the ortho/para population of interstellar  $\text{H}_2$ , which in turn provides a chemical clock for measuring the age of interstellar clouds [16, 17]. Note that the  $\text{H}_2$  ortho/para population can also be probed by observing nuclear spin populations of  $\text{H}_2\text{D}^+$  [18].

The presented work is mainly concerned with the topics of the formation of molecules and isotopic fractionation. The description of the work carried out during my post-doctoral research is organized in this thesis as follows:

- Study of the HD formation and electron transfer in the  $\text{D}^- + \text{H}$  collisions — Section 2.1, Ref. Roučka et al. [19] in Attachment A.
- Study of the isotope exchange in the  $\text{OD}^- + \text{H}_2$  collisions and dependence on the rotational state of the  $\text{H}_2$  molecule — Section 2.2.1, Ref. Roučka et al. [20] in Attachment C.
- Study of ternary association reaction of  $\text{OD}^- + \text{D}_2$  and photodetachment spectroscopy of the  $\text{D}_3\text{O}^-$  products — Section 2.2.2, Ref. Hauser et al. [21] in Attachment B.
- Investigating the formation of water in the ISM: Study of the sequence of hydrogen abstraction reactions leading from  $\text{O}^+$  to  $\text{H}_3\text{O}^+$  — Section 3.1, Refs. Tran et al. [22], Kovalenko et al. [23], and Kovalenko et al. [24] in Attachments D, E, and G.
- Investigating the formation of ammonia in the ISM:
- Studies of the rate-limiting step in the formation of ammonia in the ISM: Isotope effects and endothermicity of the  $\text{N}^+ + \text{H}_2$  reaction — Section 3.3, Refs. Plašil et al. [25] and Roučka et al. [26] in Attachments H and I.



- Study of the sequence of hydrogen abstraction reactions leading from  $\text{NH}^+$  to  $\text{NH}_4^+$  on the path towards ammonia formation — Section 3.4, Ref. [27] in Attachment F.

## 1.1 EXPERIMENTAL TECHNIQUES

This section is just a brief summary of the employed techniques. Detailed information can always be found in the referred publications and attachments.

The main body of this work was obtained using a cryogenic linear radiofrequency 22-pole ion trap (22PT) [28]. In our experimental setup, the trap is mounted on the cold head of a closed-cycle helium cryocooler and can be cooled down to trap temperatures ( $T_{22PT}$ ) between 10 K and 300 K.

The studied ions are produced by electron bombardment of a suitable precursor gas in a storage ion source [29, pp. 88], where they are also pre-cooled close to the room temperature. The produced ions are mass-selected using a linear quadrupole mass filter and injected into the trap. The ions are then stored in the trap for a predefined trapping time, during which they are thermalized to the trap temperature by collisions with a buffer gas. At the same time, the ions are undergoing collisions with the reactant gas. We estimate that the ion and reactant temperatures can be up to 10 K higher than the trap temperature and we define the collisional temperature as  $T = T_{22PT} + (5 \pm 5)$  K [22].

After the trapping time, the primary ions and reaction products are extracted from the trap, analyzed using a second quadrupole mass filter and counted using a microchannel plate detector. The efficiency of extraction and detection depends slightly on the ion mass and it is always accounted for in the data analysis (details of the analysis are described in each publication). To simplify the comparison of datasets in the plots, the numbers of detected ions  $n_x(t)$  are shown normalized by the total number of injected ions,  $n_{\Sigma 0}$  in this work.

The number densities of reactant gases are calculated from the pressure in the trap that is measured using a spinning rotor gauge. To measure pressures below the detection limit of the spinning rotor gauge, we are using a calibrated ionization gauge. The systematic uncertainty of the number density determination is estimated at 20 %.

For experiments with atomic hydrogen, we are using a hydrogen atom source (HAS) [30], where the atoms are produced in a radio-frequency discharge in pure hydrogen. The room-temperature atomic gas is then flowing through a cold capillary with a nozzle – the accommodator, where it is thermalized to the accommodator temperature  $T_{acc}$ . The accommodator can be cooled by a closed-cycle helium cryocooler to temperatures between 6 K and 300 K. Time-of-flight measurements [30, 31] have shown that, when the source is operated in the effusive regime, the translational temperature of the H atoms,

$T_H$ , closely follows the accommodator temperature and we can assume  $T_H = T_{\text{acc}}$ . When the H atoms of mass  $M_H$  are interacting with trapped ions of mass  $M_i$  and temperature  $T_i$ , the distribution of relative velocities corresponds to Maxwellian distribution with translational temperature [30]

$$T_t = \frac{M_H T_i + M_i T_H}{M_H + M_i}. \quad (1)$$

The effective number density of H atoms is determined in-situ by chemical probing. Reactions with  $\text{CO}_2^+$  and  $\text{H}^-$  have been used for calibration in the presented studies (see Refs. [19, 26, 30, 32] for details). These calibration methods have estimated systematic uncertainties of 40 % and 30 %, respectively.

During my research, I also worked on several other experimental setups, mainly in the group of prof. Roland Wester at the University of Innsbruck. These experiments include a wire octopole trap, where I participated in measurements of  $\text{CN}^-$  absolute photodetachment cross-sections [33]; a 22-pole trap with a time-of-flight mass spectrometer, where the experiments with  $\text{D}_3\text{O}^-$  formation and internal structure were carried out [21]; and finally a wire 16-pole trap [34], where I studied the process of laser photodissociation  $\text{OH}^+$  with the aim to produce a rotational-state-selected ensemble of  $\text{OH}^+$  ions in the trap (this research is still ongoing).

## 1.2 TECHNICAL DEVELOPMENTS

Besides the results in the main research field (laboratory astrophysics and molecular physics in this case), scientific work generally requires the development of new tools and techniques.

At this point, I would like to briefly mention two of these technical developments related to the topic of this thesis, which are described in dedicated publications.

The first of them is my participation in the development of the SymPy<sup>1</sup> computer algebra system written in the Python language, where I contributed an improved treatment of complex exponentiation, series expansion, and statistical distribution functions. The code, documented in Ref. [35], is widely used in the physics community as testified by the numerous references to this work.

We are also regularly designing and constructing modifications of the experiments. A recent major development is the construction of the cryogenic stationary-afterglow apparatus with cavity ring-down spectroscopy diagnostics (Cryo-SA-CRDS). For this experiment, I designed the cryogenic microwave cavity with external impedance matching and tuning to avoid the need for moving parts in the cryogenic

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<sup>1</sup> Available at <http://sympy.org>

section of the apparatus. The cavity was designed with help of numerical finite difference time domain simulations of the electromagnetic fields. These simulations were coupled with the thermal design of the discharge tube, which also influences the electromagnetic fields (a monocrystalline sapphire was chosen for high thermal conductivity and well-defined relative permittivity tensor). This development is documented in detail in Ref. [36]. Our detailed understanding of the microwave fields then allowed us to determine the number density of electrons in the plasma from the resonant frequency shift of the cavity due to the presence of electrons. This microwave diagnostics is now used as a complementary diagnostic tool to the CRDS measurement of ion number densities [37].



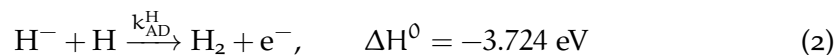
## ANIONS IN THE INTERSTELLAR MEDIUM

The presence of anions in the interstellar medium has been for a long time inferred from indirect observations and models. In 2006, the first negative ion,  $C_6H^-$ , was detected in the ISM [38] and several more were discovered in the following years (see, e.g., Ref. [39] and references therein). In addition to the spectroscopic detections in the ISM, negative ions were also observed by in the cometary comae and atmospheres of solar system bodies [40]. These discoveries motivated numerous studies investigating the role of anions in the ISM and we were able to participate in this research by studying astrophysically relevant anion processes in the ion trap instruments. The following subsections summarize the motivation and main results of our studies of anion chemistry.

### 2.1 THE $H^- + H$ AND $D^- + H$ REACTIONS AND THE FORMATION OF PROTOSTARS

There are two main motivations to studying collisions of  $H^-$  and  $H$ . The first is, that these are the simplest possible anion-neutral collisions, amenable to accurate ab-initio theoretical treatment, and experimental data can be used to benchmark these theories and in turn to gain a deeper understanding of the process. The second motivation lies in the importance of these reactions for the dynamics of the primordial gas.

In the early Universe, before the first stars were formed and started populating the ISM with heavier elements, the baryonic matter consisted almost exclusively of  $H$ ,  $Li$ , and  $He$  (including  $D$  and  $^3He$  isotopes). However, even with just three elements, the chemistry was already relatively complex with about 100 relevant processes [41, 42]. A simplified reaction network of hydrogen-helium chemistry is shown in Figure 1. It was shown [44–46] that during the formation of protostars from the primordial gas, the  $H_2$  molecule played a key role as a coolant, removing the heat from the collapsing cloud by radiative transitions. In the intermediate phases of the cloud collapse, the main channel of  $H_2$  formation was the associative detachment reaction <sup>1</sup>



<sup>1</sup> The symbol  $\Delta H^0$  indicates enthalpy change in the reaction at 0 K, i. e., the energy difference between ground state products and reactants.

*The results summarized in this section are described in detail by Gerlich et al. [32] and Roučka et al. [19, Attachment A].*

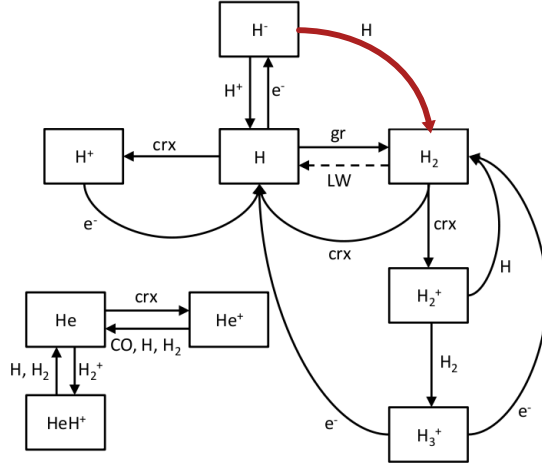
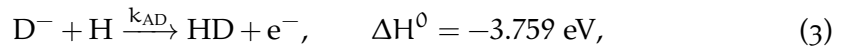


Figure 1: Hydrogen and helium reaction network. The reactants are indicated near the arrows, crx denotes cosmic ray or X-ray and LW stands for Lyman-Werner UV radiation [43]. The thick arrow indicates the associative detachment reaction (2). Adapted from Ref. [43].

and Glover et al. [46] showed that the uncertainty of its reaction rate coefficient,  $k_{AD}^H$ , is a major source of uncertainty in models of primordial star formation.

The temperature dependence of  $k_{AD}^H$  was then studied in a merged beam apparatus [47] down to about 30 K equivalent temperature. The same merged beam instrument was also used to study the fully deuterated  $D^- + D$  collision system [48], but was not capable of studying the partially deuterated  $D^- + H$  system.

We have subsequently measured the reaction rate coefficient of reaction (2) using the 22-pole trap combined with the source of atomic hydrogen at temperatures between 10 K and 135 K [32], extending and confirming the previous merged beam results. This work was already done during my Ph.D. studies and after that, we made a follow-up study of the partially deuterated variant of reaction (2)



which contributes to the formation of HD in the early Universe. The main channel of formation is, however, isotope exchange in  $D^+ + H_2$  collisions. The isotope exchange reaction is exothermic, which leads to isotope fractionation and significantly enhanced abundance of HD, relative to the natural fraction of D atoms of  $3 \times 10^{-5}$ . Since the HD molecules have a smaller spacing of rovibrational levels and stronger radiative transitions thanks to their permanent dipole moment, HD is an equally significant coolant as  $H_2$  [49]. In addition to the associative

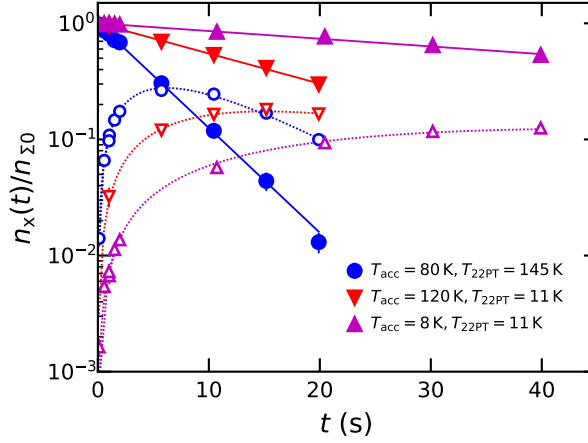
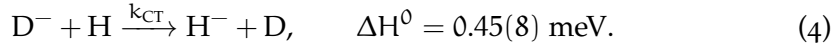


Figure 2: Time evolution of normalized numbers of detected  $\text{D}^-$  ions (filled symbols) and  $\text{H}^-$  ions (open symbols) at different combinations of  $T_{\text{acc}}$  and  $T_{22\text{PT}}$ . The solid and dashed lines show solutions of the corresponding kinetic equations fitted to the data. Adapted from Ref. [19].

detachment process (3), collisions of  $\text{D}^-$  and  $\text{H}$  can also lead to nearly resonant charge exchange



In principle, a similar charge exchange process proceeds also in the symmetric  $\text{H}^- + \text{H}$  collisions, but only isotopic tagging makes the particles distinguishable. We have measured the rate coefficients of reactions (3) and (4) at translational temperatures between 10 and 160 K. A typical sample of experimental data is shown in Figure 2. The primary  $\text{D}^-$  ions were produced by electron bombardment of  $\text{D}_2$  gas in the storage ion source and in the trap, they are destroyed by reactions (3) and (4). The  $\text{H}^-$  products of reaction (4) are detected as well and we can observe their loss due to reaction (2). The analysis of these data is described in detail by Roučka et al. [19].

In this research, we partnered with theorists from the Institute of Theoretical Physics at MFF UK, who previously successfully predicted the low-temperature rate coefficients of reaction (2) [47, 50]. In the case of the  $\text{D}^- + \text{H}$  reactions, their theoretical prediction of both associative detachment and charge exchange rate coefficients matches well the experimental data. The obtained experimental and theoretical data are summarized in Figure 3. Note that there are no previous experimental or theoretical studies of these reaction rate coefficients at energies below 4 eV (see Ref. [19] for more detailed review).

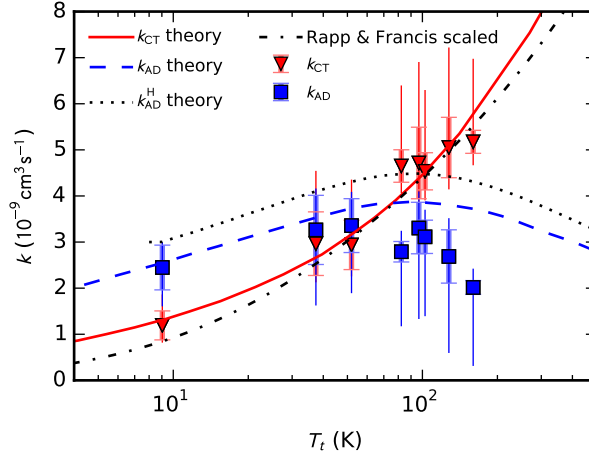


Figure 3: Rate coefficients for associative detachment ( $k_{\text{AD}}$ ) and electron transfer ( $k_{\text{ET}}$ ) in  $\text{D}^- + \text{H}$  collisions as a function of translational temperature. The experimental data are shown as squares and triangles, and the calculated results are shown as dashed and solid lines, respectively. The statistical uncertainties and the systematic uncertainties due to discrimination are indicated by the inner and outer error bars. For comparison, we show the theoretical rate coefficient of reaction (2) ( $k_{\text{AD}}^{\text{H}}$ , dotted line) and  $k_{\text{CT}}$  according to the simple theory of [51] scaled by  $1/3.6$  (dashed-dotted line). Reprinted from Ref. [19].

## 2.2 THE $\text{H}_3\text{O}^-$ REACTION COMPLEX

### 2.2.1 $\text{OD}^- + \text{H}_2$ Isotope Exchange

*The results summarized in this section are described in detail by Mulin et al. [52] and Roučka et al. [20, Attachment C].*

Before diving into the discussion of the  $\text{OD}^- + \text{H}_2$  reaction, we have to briefly introduce the internal structure of the  $\text{H}_2$  molecule, which can exist in two nuclear spin configurations — ortho- $\text{H}_2$  and para- $\text{H}_2$ . The  $1/2$  spins of the nuclei can add up to total nuclear spin  $I = 1$  (ortho- $\text{H}_2$ , statistical weight 3), or  $I = 0$  (para- $\text{H}_2$ , statistical weight 1). Hydrogen with a statistical mixture (3 : 1) of ortho and para states is called normal hydrogen. Due to the Pauli exclusion principle, the symmetric (ortho) nuclear spin states must be combined with anti-symmetric rotational wave functions (odd  $J$ ) and vice versa, ortho- $\text{H}_2$  has even  $J$ . The spontaneous transitions between ortho and para configurations are extremely rare [53] and therefore, ortho- and para- $\text{H}_2$  are often considered as separate species in astrochemical models [54]. One of the key differences between these nuclear spin isomers is the difference in their rotational energies, where the lowest ortho state is in  $J = 1$  level with rotational energy of 15 meV. This relatively small rotational energy can significantly influence its reactivity in weakly exothermic reactions, as will be illustrated below, and also in Section 3.3.



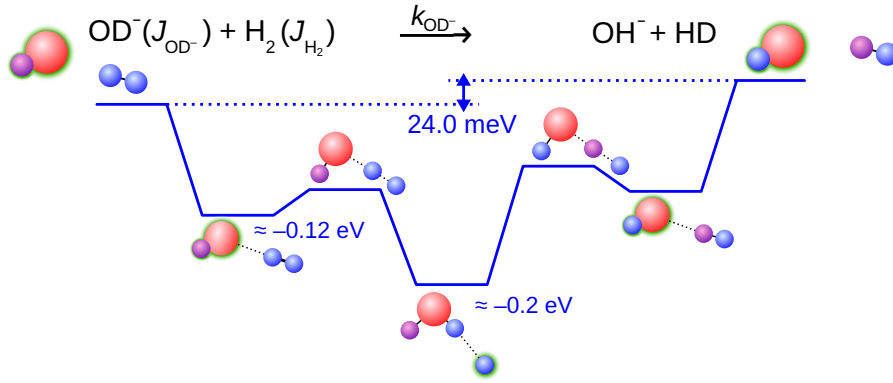
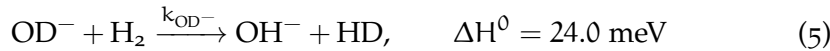


Figure 4: Schematic potential energy diagram of reaction 5. The reaction proceeds via intermediate complexes OD<sup>-</sup>·(H<sub>2</sub>), H<sup>-</sup>·(DOH), and OH<sup>-</sup>·(HD). The intermediate complex energies are taken from [57] and corrected for approximate vibrational zero point energies [58].

At this point, we should also mention that the vibrationally excited states of H<sub>2</sub> have a relatively long lifetime [55] and can contribute to driving endothermic reactions in the ISM as well (see, e. g., Ref. [56]). Studies of reactivity of vibrationally excited H<sub>2</sub> with C<sup>+</sup> ions is one of the subjects of my ongoing research project.

The isotope exchange reaction



is a weakly endothermic process, which leads to the destruction of OD<sup>-</sup> ions. The endothermicity is comparable to the rotational energy of H<sub>2</sub>(J = 1) and therefore, a significant dependence on the ortho / para ratio of H<sub>2</sub> can be expected. The reaction proceeds via three intermediate complexes and two transition states as illustrated in Figure 4.

The OH<sup>-</sup> and OD<sup>-</sup> ions have not been observed in the ISM yet, but OD<sup>-</sup> is considered to be a candidate for detection [59] and astrochemical models [60] predict the presence of OH<sup>-</sup> in quantities comparable to those of OH<sup>+</sup>. Besides their astrochemical relevance, the OH<sup>-</sup> and OD<sup>-</sup> ions have recently been a subject to a number of theoretical and experimental studies [21, 59, 61–67] and are being used as tool for thermometry of ions in ion traps and storage rings [68–71].

Previous experimental studies of Reaction (5) were only done with normal hydrogen at temperatures above 100 K [72, 73] and we are not aware of any theoretical calculations of the rate coefficients of the reaction (5). We first extended the measurements of reaction with normal hydrogen down to 10 K in the study of Mulin et al. [52], which was also concerned with isotope exchange in the reaction



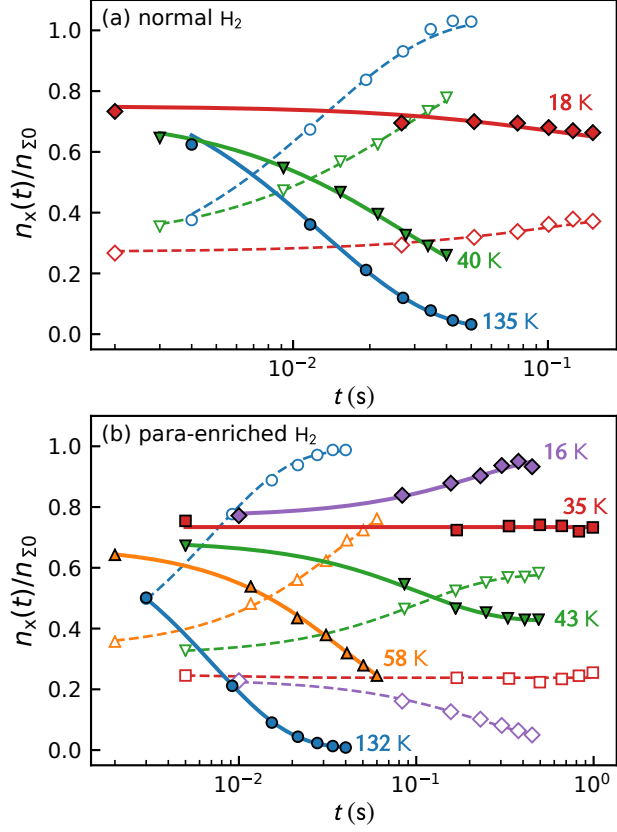


Figure 5: The evolution of normalized numbers of trapped OD<sup>-</sup> ions (full symbols) and OH<sup>-</sup> ions (open symbols). The ions are subject to interaction with normal and para-enriched H<sub>2</sub> in the upper and lower panel, respectively. See text and Ref. [20] for more details. Adapted from Ref. [20].

In the follow-up study by Roučka et al. [20], we studied the influence of rotational excitation on the rate coefficient of reaction (5).

The OD<sup>-</sup> ions were produced by electron bombardment of a mixture of N<sub>2</sub>O and D<sub>2</sub> in the storage ion source. The para-enriched hydrogen was produced by catalytic conversion of normal hydrogen at temperatures below 20 K using Fe<sub>2</sub>O<sub>3</sub> as a paramagnetic catalyst [74]. We determined by in-situ calibration with the N<sup>+</sup> + H<sub>2</sub> reaction [75] that the fraction of para-H<sub>2</sub> in the trap is 99.5 %.

We observed (as expected for endothermic reaction) that the reaction with para-enriched hydrogen is extremely slow at low temperatures. Figure 5 shows typical time evolutions of the number of trapped OD<sup>-</sup> and OH<sup>-</sup> ions at various temperatures. The measurements in each panel of the figure were obtained at the constant flow of reactant gas, which means that the reactant number density is proportional to  $1/\sqrt{T}$ . At low temperatures, the conversion of OD<sup>-</sup> to OH<sup>-</sup> in reaction (5) is competing with back-conversion in reaction (6) with the small amount of D<sub>2</sub> coming from the ion source. This process must be accounted for in the data analysis (see Ref. [20] for details).

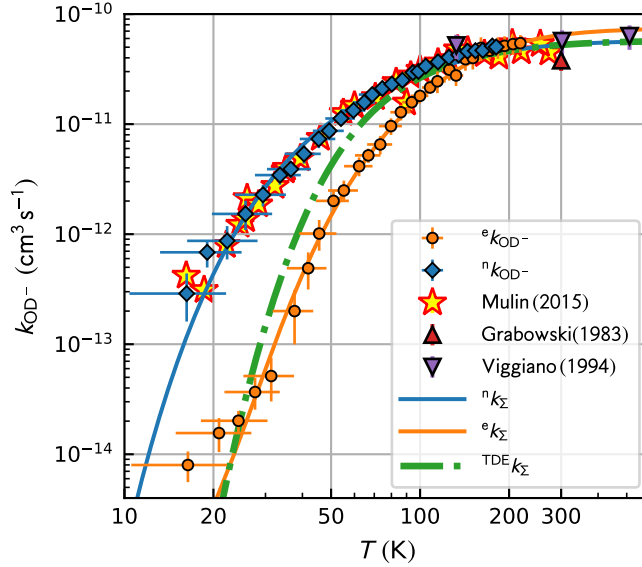


Figure 6: Temperature dependencies of the rate coefficients  ${}^n k_{\text{OD}^-}$  and  ${}^e k_{\text{OD}^-}$  of reaction (5) obtained with normal and para-enriched  $\text{H}_2$  as a reactant [20]. The results are compared to  ${}^n k_{\text{OD}^-}$  obtained in our previous study by Mulin et al. [52], and by Grabowski et al. [72] and Viggiano and Morris [73]. See text for details. Adapted from Ref. [20].

The temperature dependence of the obtained rate coefficients of reaction with ortho- and para- $\text{H}_2$  is shown in Figure 6. We analyzed the data by fitting with a statistical model that assumes Arrhenius-like dependence for every state-to-state reaction rate coefficient with activation energy reduced by the internal excitation of reactants (see Ref. [20] for details). The corresponding fits of our data by this model for reactions with normal ( ${}^n k_{\Sigma}$ ) and para-enriched ( ${}^e k_{\Sigma}$ )  $\text{H}_2$  are indicated by the solid lines and the evaluated thermal rate coefficient  ${}^{\text{TDE}} k_{\Sigma}$  by the dash-dotted line in Figure 6. The reaction endothermicity estimated from the fits is

$$\Delta H_{\text{fit}}^0 = 25.3_{-2.1}^{+2.4} \text{ meV}, \quad (7)$$

in good agreement with the theoretical value of  $\Delta H^0 = 24.0 \text{ meV}$ . Comparison with the activation energy  $E_A$  determined from simple Arrhenius fits with a function  $k(T) = A \exp(-E_A/k_B T)$  in Ref. [20] shows  $E_A$  is a less accurate estimate of the reaction endothermicity in this case. The statistical model is a suitable and relatively simple method for the estimation of reaction endothermicities.

### 2.2.2 Formation, Destruction, and Internal structure of $\text{D}_3\text{O}^-$

An interesting aspect of the  $\text{H}_3\text{O}^-$  collision complex is, that it can be stabilized by collision with a third body and since there are two

*The results summarized in this section are described in detail by Hauser et al. [21, Attachment B].*

distinct minima on the potential energy surface (PES) (see Figure 7 or Figure 4, disregarding the isotope differences), there is a possibility of forming two distinct isomers,  $\text{H}^- (\text{H}_2\text{O})$  and  $\text{H}_2^- (\text{OH})$ .

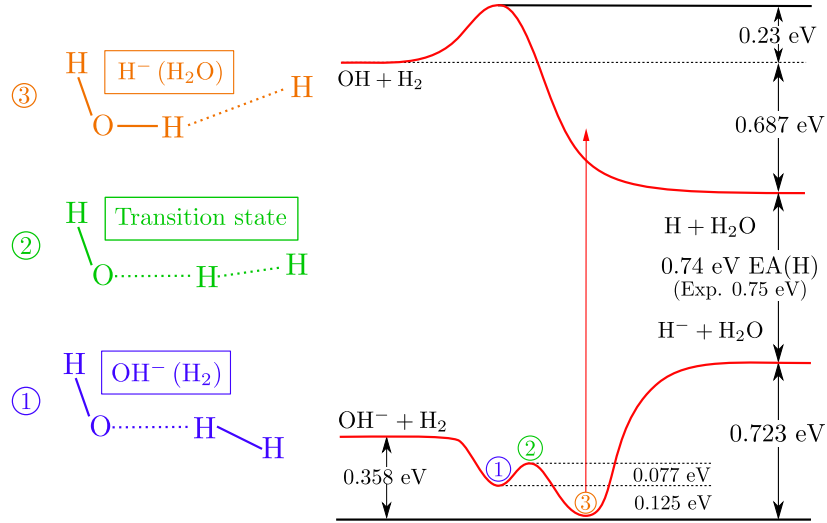
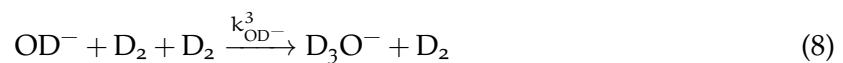


Figure 7: One-dimensional cut of the Born-Oppenheimer PES of  $\text{H}_3\text{O}^-$  and  $\text{H}_3\text{O}$  showing the different isomers. The studied photodetachment transition is indicated by the arrow. Reprinted from Ref. [21].

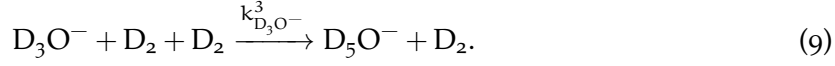
Note that a similar problem arises also in collisions of  $\text{O}^-$  with  $\text{H}_2$ , where a weakly bound  $\text{H}_2\text{O}^-$  complex can be formed in a local minimum, but there, the global minimum is actually above the PES of neutral  $\text{H}_2\text{O}$ , which leads to electron detachment. We have studied the collisions of  $\text{O}^-$  with  $\text{H}_2$  and  $\text{D}_2$  in collaboration with theorists from the Institute of Theoretical Physics at our faculty and currently we are analyzing the results of a study of  $\text{O}^- + \text{HD}$  collisions (see Refs. [62, 63] for details of the  $\text{O}^- + \text{H}_2 / \text{D}_2$  studies).

Previous theoretical calculations of the  $\text{H}_3\text{O}^-$  vibrational structure have shown [57, 76] that the different isomers are not truly separated by the barrier due to their vibrational zero point energies, but there are localized vibrational states in each minimum. One of the aims of our study was to determine, whether some fraction of  $\text{D}_3\text{O}^-$  produced in a ternary association reaction is in the form of long-lived  $\text{D}_2^- (\text{OD})$  isomer. We used  $\text{D}_3\text{O}^-$  instead of  $\text{H}_3\text{O}^-$  mainly to avoid parasitic deuteration reactions, but the smaller zero-point energy of the heavier isotope may even lead to a higher significance of the potential barrier. We are not aware of any calculation of  $\text{D}_3\text{O}^-$  vibrational structure.

The experiments described below were carried out during my stay in the group of prof. Wester at the University of Innsbruck. We first studied the formation of  $\text{D}_3\text{O}^-$  in the ternary association reaction



and its destruction in subsequent ternary association towards  $\text{D}_5\text{O}^-$



Previously, reaction (8) has only been studied with  $\text{H}_3\text{O}^- + \text{H}_2$  isotopes at temperatures above 88 K by Miller et al. [77]. As expected, we observed quadratic dependence of the reaction rates on the reactant number density and from a least squares fit of this dependence, we obtained the following values of the ternary association rate coefficients at 20 K (statistical and systematic uncertainties are indicated)

$$k_{\text{OD}^-}^3 = (3.3 \pm 0.2^{\text{stat}} \pm 0.3^{\text{sys}}) \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}, \quad (10)$$

$$k_{\text{D}_3\text{O}^-}^3 = (2.4 \pm 0.1^{\text{stat}} \pm 0.2^{\text{sys}}) \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}. \quad (11)$$

To resolve the internal structure of the  $\text{D}_3\text{O}^-$  ions produced in the trap, we illuminated the stored ions by a laser with photon energy of 1.82 meV. As illustrated in Figure 7, the energy difference between neutral and anionic PES is smaller in the global minimum than in the local minimum of the  $\text{D}_3\text{O}^-$  PES. Therefore, also the photodetachment threshold energy of  $\text{D}_3\text{O}^-$  is lower for the ground state isomer. It was estimated in previous photodetachment studies that the electron binding energy of the  $\text{OD}^-$  ( $\text{D}_2$ ) and  $\text{D}^-$  ( $\text{D}_2\text{O}$ ) is 2.05 eV and 1.5 eV, respectively. Therefore, the applied light should only destroy the  $\text{D}^-$  ( $\text{D}_2\text{O}$ ) form of  $\text{D}_3\text{O}^-$ . However, we observed that switching on the laser leads to a monoexponential decay of the number of ions and a complete depletion of the  $\text{D}_3\text{O}^-$  ion signal. This means that the  $\text{OD}^-$  ( $\text{D}_2$ ) isomer is not stable (on the second time scale) in the conditions of the presented ion trap experiment.



## GAS-PHASE FORMATION OF HYDRIDES

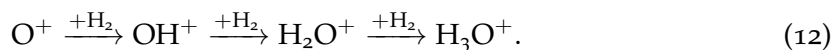
Interstellar hydrides are simple molecules that stand at the beginning of molecular synthesis in the interstellar clouds [78]. The most abundant types are carbon, nitrogen, and oxygen hydrides and in this work, we investigate in detail the gas-phase formation of the latter two types. In particular, we are concerned with sequences of hydrogen abstraction reactions that lead to formation of  $\text{H}_3\text{O}^+$  and  $\text{NH}_4^+$  ions from  $\text{O}^+$  and  $\text{N}^+$ , respectively, as illustrated in the chemical network in Figure 8. The  $\text{H}_3\text{O}^+$  and  $\text{NH}_4^+$  ions can subsequently dissociatively recombine with electrons to produce interstellar water and ammonia. Our study of the formation of the oxygen hydride ions in a sequence of fast hydrogen abstraction reactions is described in the following Section 3.1. With nitrogen hydrides, the situation is slightly more complicated, because the formation of nitrogen hydride ions starts with a reaction of  $\text{N}^+$  with  $\text{H}_2$ , which has a small activation energy, but its actual endothermicity has not been determined in any previous study.

Our results concerning the formation of nitrogen hydride ions and the endothermicity of the  $\text{N}^+ + \text{H}_2$  reaction are discussed in Section 3.2.

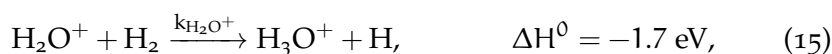
Since the observed number densities of oxygen and nitrogen hydrides are regularly used as tracers for other quantities such as local ionization rate, a fraction of molecular/atomic hydrogen, ortho/para ratio of  $\text{H}_2$ , etc. [78–84], more accurate rates of their formation and destruction should also improve the accuracy of the derived quantities.

## 3.1 PATHWAY TO WATER FORMATION IN THE ISM

The main pathway to the gas-phase formation of water in the ISM leads through a sequence of hydrogen abstraction reactions



followed by dissociative recombination of  $\text{H}_3\text{O}^+$  with electrons. The exothermic reactions of this sequence<sup>1</sup>



<sup>1</sup> see Ref. [22] for details of the endothermicity evaluation

*The results summarized in this section are described in detail by Kovalenko et al. [23, Attachment E], Kovalenko et al. [24, Attachment G], Tran et al. [22, Attachment D].*

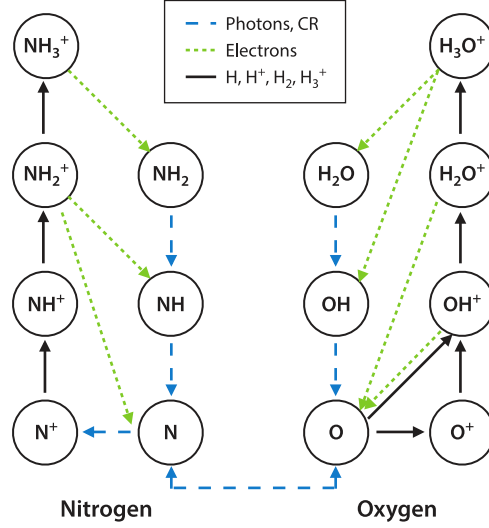
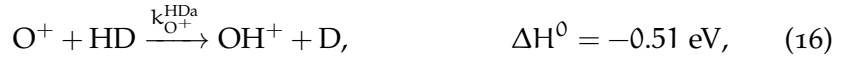


Figure 8: The UV-driven chemical network initiating the oxygen and nitrogen chemistry in the ISM. The reactants are indicated by the arrow types (see the legend and Ref. [78] for details, CR denotes cosmic rays). Adapted from Ref. [78].

have been studied previously in a number of experiments at 300 K or at higher temperatures (see Refs. [85–92]. First low-temperature studies of reactions (14) [93] and (15) [94] at temperatures down to 200 K and 100 K, respectively, have been published relatively recently. We have studied the whole sequence of hydrogen abstraction reactions (12) in the 22-pole ion trap at temperatures down to 10 K [22, 23] and nearly simultaneously with us, another study of reactions (14) and (15) at cryogenic temperatures was performed in the 22-pole trap apparatus in Heidelberg [95]. A comparison of results of these two independent studies will be presented below. Note that the  $O^+$  ions can exist in long-lived metastable electronic states  $O^+(^2D)$  and  $O^+(^2P)$  that are not easily quenched by collisions with the helium buffer gas. We measured the fraction of these metastable ions by in-situ chemical probing to make sure that the measured rate coefficients correspond to the reaction of ground state  $O^+(^4S)$  (see Ref. [23] for details).

In addition to the reactions with  $H_2$ , we have also studied the isotopic effects and branching ratios related to deuteration in the following reactions with  $O^+$



and the results of this work are published in Ref. [24].

We present a small sample of the obtained results in the form of temperature-dependent rate coefficients of reactions (14) and (15) and



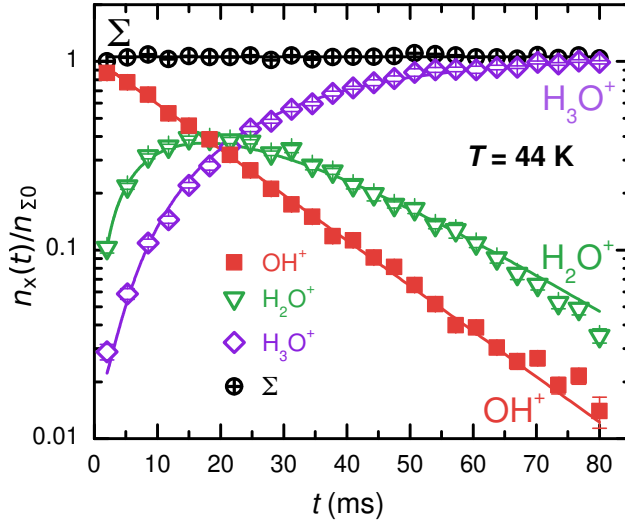


Figure 9: Time evolution of the normalized numbers ions after injecting  $\text{OH}^+$  ions into the trap filled with  $[\text{H}_2] = 6.4 \times 10^{10} \text{ cm}^{-3}$  at 44 K temperature. The experimental data are indicated by points and the fitted kinetic model is indicated by the solid lines. The total number of ions ( $\Sigma$ ) is also indicated. Adapted from Ref. [22].

we refer the reader to the relevant publications [22–24] for more detail.

An example of raw experimental data obtained after injecting  $\text{OH}^+$  ions into the trap is shown in Figure 9. The evaluated reaction rate coefficients of reactions (14) and (15) are presented in Figures 10 and 11. Our data are compared to the results of previous experiments: selected ion flow tube (SIFT-a [90] and SIFT-b [91]), flowing afterglow (FA [87]), ion cyclotron resonance ion trap (ICR [96]), variable-temperature SIFT (VT-SIFT [93, 94]), flow-drift tube (FDT [92]), and double-quadrupole double-octopole (DQDO [97]).

The new results from the low-temperature ion trap experiment by Kumar et al. [95] are also indicated in the plots. Their reaction rate coefficients are systematically higher than our results, but the difference is within the indicated systematic uncertainties, confirming the reliability of both results.

With the data presented in this section (and the corresponding papers [22–24]), we have significantly extended the temperature range of experimentally determined rate coefficients relevant to the formation and deuterium fractionation of oxygen hydride ions and water in the ISM. We expect that the incorporation of these data will improve the reliability of astrochemical models.

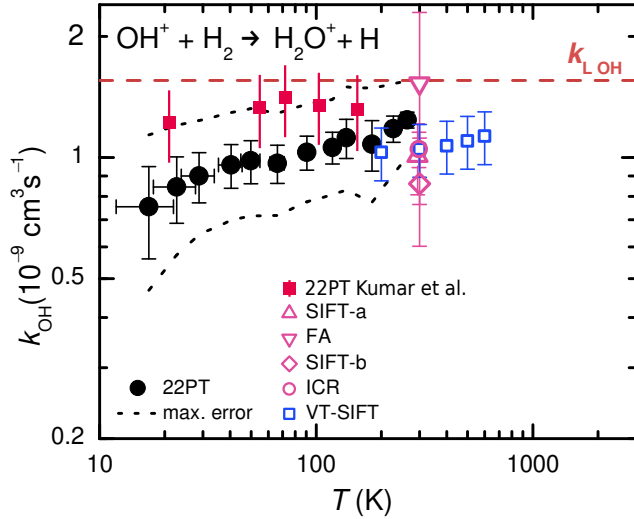
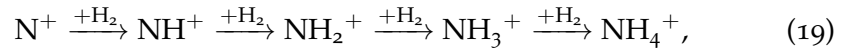


Figure 10: Temperature dependence of the rate coefficient of reaction (14). The data obtained in our study [22] are indicated by filled circles. Their statistical errors and errors due to temperature uncertainty are indicated by the error bars and the total systematic uncertainty is indicated by the dashed line. Error bars of other data indicate the total uncertainty. See text for a description of the other data. Adapted from Ref. [22].

### 3.2 PATHWAY TO AMMONIA FORMATION IN THE ISM

A major part of my post-doctoral work consisted of studying the gas-phase formation of ammonia,  $\text{NH}_3$ , in the ISM. The current understanding is [78, 79, 98], that  $\text{NH}_3$  is mainly a product of the dissociative recombination of  $\text{NH}_4^+$  with electrons, where  $\text{NH}_4^+$  is produced in a chain of hydrogen abstraction reactions



followed by dissociative recombination of  $\text{NH}_4^+$ . The  $\text{N}^+$  ions are produced in dissociative ionization of  $\text{N}_2$  by  $\text{He}^+$  [79]. The rate-limiting step in this chain of reactions at the low temperatures of the interstellar medium is the first hydrogen abstraction reaction of  $\text{N}^+$  with  $\text{H}_2$ , which has a significant activation energy. Therefore, this reaction was the main focus of our work. We studied various isotopic variants of this reaction in order to gain a better understanding of the isotopic effects and energetics and we also measured the rate coefficient of the reverse reaction of  $\text{NH}^+$  with H atoms in order to evaluate the reaction endothermicity (see Section 3.3 below).

We also studied the remaining hydrogen abstraction reactions of  $\text{NH}^+$ ,  $\text{NH}_2^+$ , and  $\text{NH}_3^+$  with  $\text{H}_2$  in order to provide more accurate and reliable low-temperature reaction rate coefficients for use in astrochemical models (see Section 3.4).

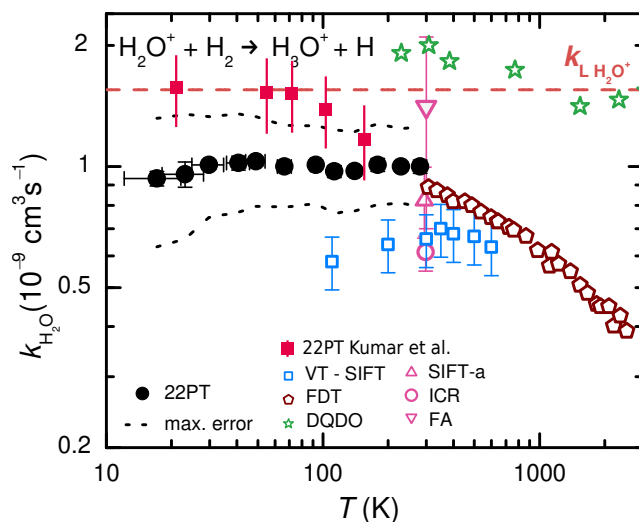


Figure 11: Temperature dependence of the rate coefficient of reaction (15). The data obtained in our study [22] are indicated by filled circles. Their statistical errors and errors due to temperature uncertainty are indicated by the error bars and the total systematic uncertainty is indicated by the dashed line. Error bars of other data indicate the total uncertainty. See text for a description of the other data. Adapted from Ref. [22].

### 3.3 THE $\text{N}^+ + \text{H}_2 \longrightarrow \text{NH}^+ + \text{H}$ REACTION

For a long time, it has been known that the reaction



has a small activation energy of approximately 17 meV (see, e. g., Zymak et al. [75]), but it was not clear, whether this activation energy is caused by actual reaction endothermicity or a barrier on the reaction path [99, 100]. Numerous experimental studies of this reaction system and its isotopic variants do not provide a conclusive answer to this question [75, 99–103]. The endothermicity cannot be calculated from theoretical molecular parameters either, as the binding energy of  $\text{NH}^+$  is not yet known with sufficient precision [104], although, recent advances in the theoretical studies and spectroscopy of the  $\text{NH}^+$  ion may soon provide sufficiently accurate dissociation energy [105–110].

#### 3.3.1 Isotope Effects

Some understanding of the reaction energetics can be gained by observing, how various forms of energy influence the reaction rate coefficient. The most straightforward method consists of measuring the temperature dependence of thermal reaction rate coefficients. The

*The results summarized in this section are described in detail by Plašil et al. [25, Attachment H].*

available energy can also be modified by studying the reaction with normal and para-enriched H<sub>2</sub> [75, 99, 103] and with different isotopic variants [99, 101–103]. If the activation energy is caused by reaction endothermicity, the change of activation energy due to isotope replacement should just correspond to the change of the vibrational zero-point energy (ZPE) of products minus the change of ZPE of reactants and similarly in case of rotational excitation.

Studies of this type have been done previously in GIB (guided ion beam) [102, 111], CRESU (Cinétique de Réaction en Écoulement Supersonique Uniforme) Marquette et al. [103], SIFDT (selected ion flow-drift tube) [101], merged and crossed beams [100], and in the 22-pole ion trap (22PT) [75, 99] experiments.

However, some of the previous studies found significant deviations from this expected behavior [99, 100]. In order to elucidate this issue, we have measured the temperature dependence of the rate coefficients of the reactions



at temperatures down to 10 K [25] and compared them with the rate coefficients of the reaction with normal and para-enriched H<sub>2</sub> obtained previously [75]. An example of experimental data showing the time evolution of numbers of ions after injecting N<sup>+</sup> into the trap filled with 3.3 × 10<sup>11</sup> cm<sup>-3</sup> of D<sub>2</sub> at 209 K collisional temperature is shown in Figure 12.

The data were analyzed as usual by least-squares fitting of the time dependence with a model of chemical kinetics to obtain the reaction rate coefficients. To improve the accuracy of our results, we determined by CRDS spectroscopy the fraction of HD impurity in the D<sub>2</sub> gas and we corrected the reaction rate coefficients for the known contribution of reactions with HD (as determined in the same study, the procedure is described in detail in Ref. [25]). The temperature dependence of  $k_{\text{N}^+}^{\text{D}_2}$  is shown in Figure 13 in comparison with the results of previous studies. The significantly higher low-temperature reaction rate coefficients obtained in Refs. [99, 103] were caused by the admixture of HD in the D<sub>2</sub> gas.

The HD data were analyzed in a similar manner. The branching ratios for the production of ND<sup>+</sup> and NH<sup>+</sup> were evaluated from the fits in addition to the total reaction rate coefficient. We also took into account the contribution of normal H<sub>2</sub> present in the HD gas in the evaluation of the reaction rate coefficients and their uncertainties. The data for both reaction channels are summarized in Figure 14.

In order to facilitate the comparison of endothermicities of different isotopic variants of reaction (20), we define the so-called vibrationless

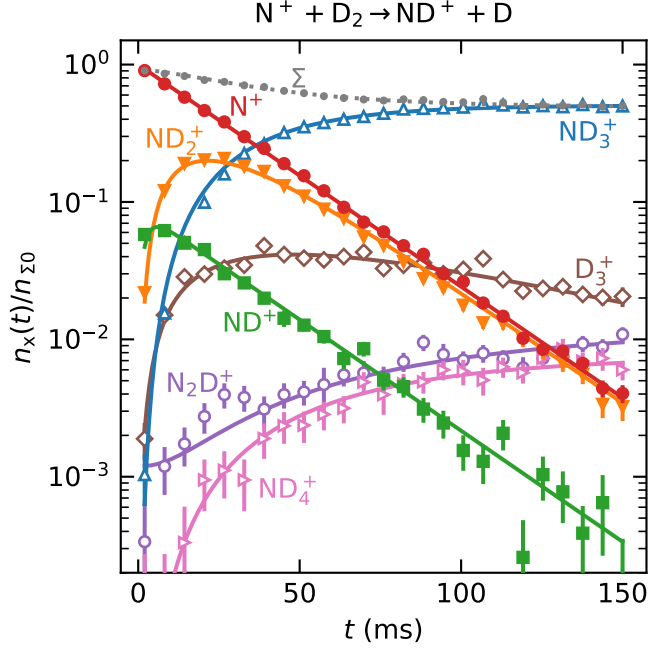


Figure 12: Time evolution of the normalized numbers of trapped ions after injecting  $\text{N}^+$  into the trap filled with  $3.3 \times 10^{11} \text{ cm}^{-3}$  of  $\text{D}_2$  at 209 K collisional temperature. Nitrogen hydrides  $\text{ND}^+$ ,  $\text{ND}_2^+$ ,  $\text{ND}_3^+$ , and  $\text{ND}_4^+$  are produced in the sequence of hydrogen abstraction reactions. Small fraction of  $\text{D}_3^+$  is produced in the reaction of  $\text{ND}^+$  with  $\text{D}_2$  [27] and these ions are converted to  $\text{N}_2\text{D}^+$  in reactions with  $\text{N}_2$  coming from the ion source. Reprinted from Ref. [25].

energy change  $\Delta E_e$  as the difference of equilibrium electronic potential energies of reactants and products. In the Born-Oppenheimer approximation (BOA) it can be simply obtained by correcting the 0 K endothermicity  $\Delta H^0$  for vibrational zero-point energies (ZPE) of reactants and products, expressed symbolically as

$$\Delta E_e = \Delta H^0 - \text{ZPE}(\text{reactants}) + \text{ZPE}(\text{products}). \quad (24)$$

Within BOA, this quantity is isotope-independent. To improve the accuracy of our comparison beyond the BOA, we include the experimentally determined isotope shifts of HD,  $\text{D}_2$ , and D and approximate adiabatic corrections for  $\text{ND}^+$ . We also take into account the non-equilibrium rotational populations of  $\text{H}_2$  and  $\text{D}_2$  reactants (see Ref. [25] for detailed information). In our initial analysis, we calculated the activation energies of each studied reaction variant by fitting the temperature dependence of its rate coefficient with Arrhenius dependence  $k(T) = A \exp(-E_A/k_B T)$ . The corresponding values of  $\Delta E_e$  obtained by treating these activation energies  $E_A$  as endothermicities (i. e., assuming there are no energy barriers<sup>2</sup>) are compared

<sup>2</sup> Interpretation of Arrhenius activation energies as endothermicities is generally valid for barrierless reactions in the low-temperature limit,  $T \ll E_A/k_B$ . At intermediate

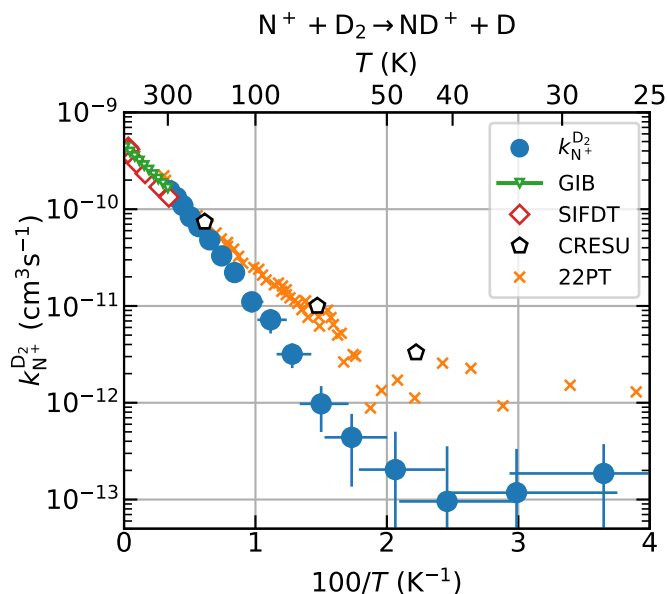


Figure 13: Arrhenius plot of the rate coefficients  $k_{N^+}^{D_2}$  of reaction (23). The present data (filled circles) are compared with previous results of SIFDT [101], GIB [102], CRESU [103], and 22PT [99] experiments. Adapted from Ref. [25].

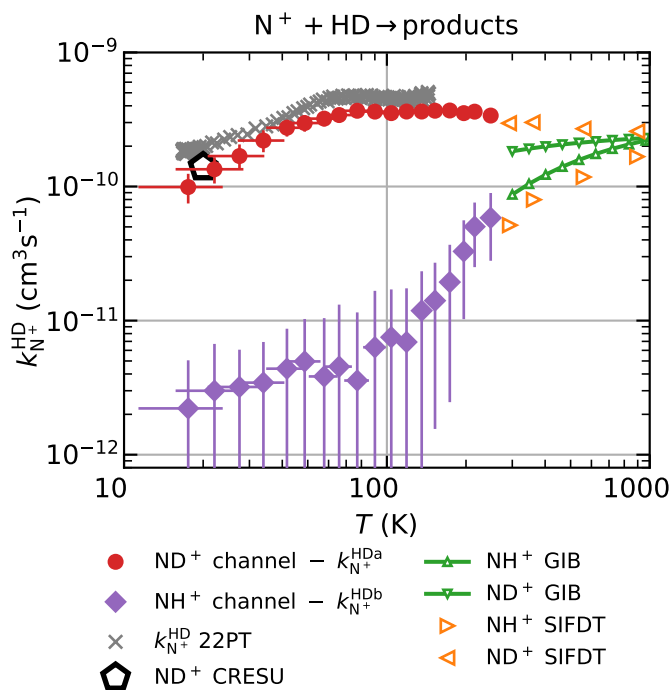


Figure 14: Temperature dependence of the rate coefficients of reactions (21), and (22). The present data (filled circles and diamonds) are compared with the results of previous SIFDT [101], GIB [102], and CRESU [103] experiments. The total rate coefficient  $k_{N^+}^{HD} = k_{N^+}^{HDa} + k_{N^+}^{HDb}$  obtained in the 22PT experiment [112] is also shown for comparison. Adapted from Ref. [25].

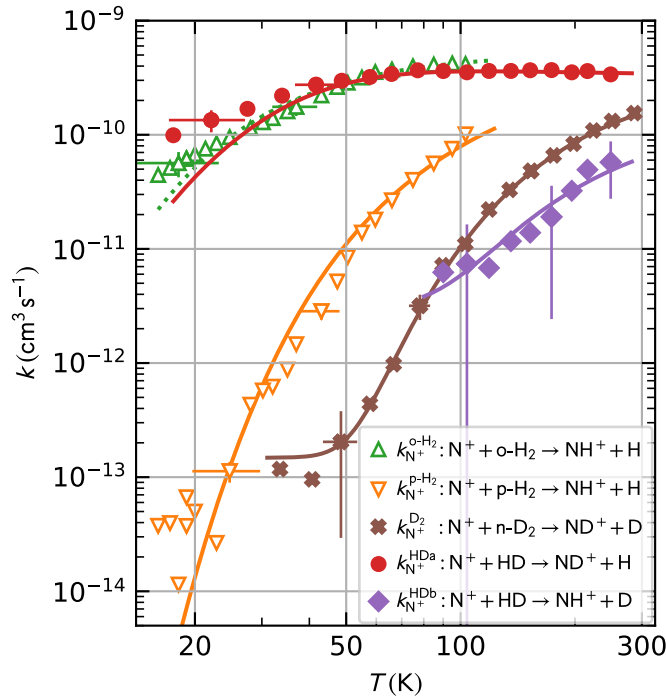


Figure 15: Overview of the available low-temperature rate coefficients of reactions (20), (21), (22), and (23). The rate coefficients of reactions with para- and ortho- $\text{H}_2$  are indicated as  $k_{\text{N}^+}^{\text{p-H}_2}$  and  $k_{\text{N}^+}^{\text{o-H}_2}$  in the legend, respectively. The results of the fitted global model are indicated by the solid lines. Reprinted from Ref. [25].

to results obtained in previous studies in Figure 21. It can be seen that the values obtained from the Arrhenius fits in Ref. [25] are mutually compatible. The large discrepancy that was previously observed in the case of the  $\text{N}^+ + \text{D}_2$  data is not present in our analysis of the low-temperature data.

To evaluate the reaction endothermicity more accurately, we developed a statistical model that takes into account the internal excitation of reactants and the shape of the cross-section near the threshold. We model each of the studied reaction rate coefficients as a sum of state-to-state coefficients. The threshold energy of each channel is calculated from a common isotope-independent value of  $\Delta E_e$ , assuming the absence of energy barriers. The isotope electronic shifts, which are on the order of several meV, are also taken into account. The model was fitted globally to all the low-temperature ion trap data using the orthogonal distance regression [114] in order to treat the temperature uncertainty properly. The agreement of the model with the rate coefficients of reactions with HD,  $\text{D}_2$ , ortho- $\text{H}_2$ , and para- $\text{H}_2$  can be appreci-

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temperatures, the value of  $E_A$  is influenced by the interaction of excited states and by the shape of the cross-section near the threshold [113]. We account for these effects in the statistical model described below and in Ref. [25].

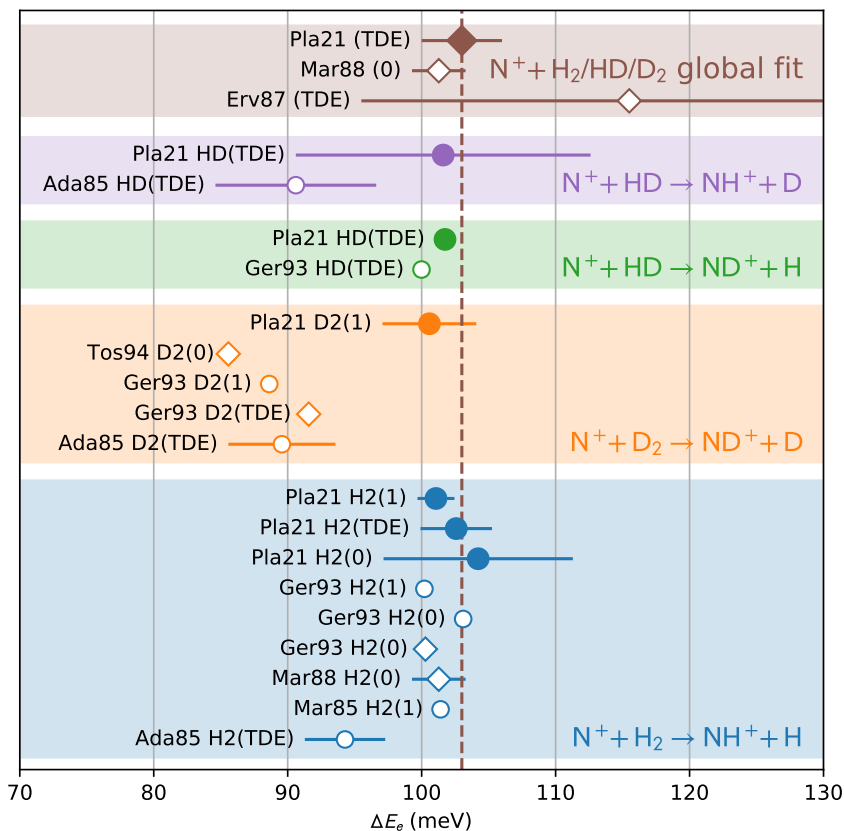


Figure 16: Summary of the values of  $\Delta E_e$  evaluated from the data of previous and present studies of isotopic variants of reaction (20). The values obtained directly from activation energies are indicated by circles (Pla21 [25], Ger93 [99], Ada85 [101], Mar85 [115]), whereas the diamonds indicate data evaluated using a more advanced model — either statistical state-to-state threshold cross section model (Erv87 [102], Mar88 [103], Pla21 [25]), or a phase space theory calculation (Ger93 [99], Tos94 [100]).

ated from Figure 15. The data for ortho- and para- $H_2$  were evaluated from the measurements with normal and para-enriched  $H_2$  by Zymak et al. [75]. Statistical goodness-of-fit tests show that this model is compatible with our data (which can be considered the most accurate low-temperature data available). The comparison in Figure 16 shows that the value of  $\Delta E_e$  obtained using the statistical model is in good agreement with the values from Arrhenius fits.

Note that the previous studies indicating the presence of energy barriers [99, 100] did not estimate the uncertainties of their endothermicity determination. It is therefore not easily possible to judge the statistical significance of their observation and perhaps, the discrepancy can be explained by a relatively small systematic uncertainty of temperature and isotopic impurities that were not accounted for in the previous studies. This can be seen in the case of the  $N^+ + D$  re-



action (Figure 13), where the contribution of HD and possibly also insufficient thermalization visibly influences the previous data.

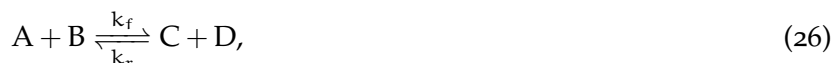
The main outcome of this study is, apart from providing more accurate data for astrochemical modeling, the conclusion that there is no significant evidence for the presence of barriers in the studied set of reactions.

### 3.3.2 Reverse Reaction and Endothermicity Analysis

A general and reliable method for experimental determination of reaction endothermicity consists of measuring the rate coefficient of the studied reaction and of its reverse process at the same temperature. The ratio of the forward and reverse reaction rate coefficients — the equilibrium constant  $K_{\text{eq}}$  — is related to the reaction endothermicity due to the principle of detailed balance (see, e.g., pages 307–313 in Ref. [116] for derivation from first principles). We, therefore, set out to measure the rate coefficient of the reverse reaction



In the general formulation of the detailed balance principle for a binary reaction



the forward and reverse reaction rate coefficients,  $k_f$  and  $k_r$  are related by the formula

$$\frac{k_f}{k_r} = \left( \frac{\mu_{\text{CD}}}{\mu_{\text{AB}}} \right)^{3/2} \frac{q_{\text{C}} q_{\text{D}}}{q_{\text{A}} q_{\text{B}}} \exp \left( -\frac{\Delta H^0}{k_{\text{B}} T} \right) \equiv K_{\text{eq}}, \quad (27)$$

where the symbol  $q_X$  denotes the internal partition sum of species  $X$ ,  $\mu_{XY}$  is the reduced mass of species  $X$  and  $Y$ ,  $K_{\text{eq}}$  is the equilibrium constant, and  $\Delta H^0$  is the energy difference between the ground states of products and reactants (see, e.g., page 313 in Ref. [116]). The general partition sum over internal states can be written as  $q_X = \sum_i g_{iX} \exp(-E_{iX}/k_{\text{B}}T)$ , where  $g_{iX}$  and  $E_{iX}$  are the state multiplicities and energies relative to the ground state, respectively.

If we apply the detailed balance principle (27) to forward and reverse reactions (20) and (25), the 0 K endothermicity of reaction (20) can be evaluated as

$$\Delta H^0 = k_{\text{B}} T \ln \left( \left( \frac{\mu_{\text{NH}^+, \text{H}}}{\mu_{\text{N}^+, \text{H}_2}} \right)^{3/2} \frac{k_r q_{\text{NH}^+} q_{\text{H}}}{k_f q_{\text{N}^+} q_{\text{H}_2}} \right). \quad (28)$$

Our calculation of the partition functions, including the relevant electronic, rotational, fine structure, and hyperfine structure effects, is described in detail in Ref. [26]. The relatively complicated structure

*The results summarized in this section are described in detail by Roučka et al. [26, Attachment I].*

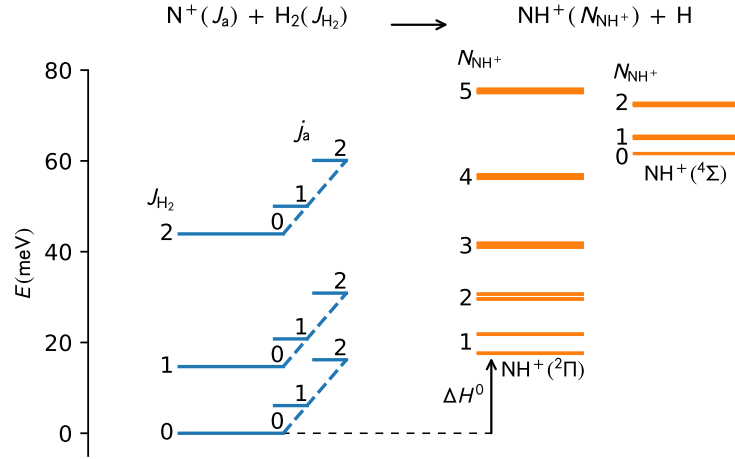


Figure 17: Energy levels of the  $\text{NH}_2^+$  reaction system. The energies of the reactant configuration as a function of  $\text{N}^+$  fine structure state ( $j_a$ ) and  $\text{H}_2$  rotational state ( $J_{\text{H}_2}$ ) are indicated on the left. The energies of the product system as a function of  $\text{NH}^+$  rotational state are shown for the two lowest electronic states of  $\text{NH}^+$ . The rotational states of  $\text{NH}^+$  are labeled by the rotational angular momentum quantum number  $N_{\text{NH}^+}$ . See Ref. [26] for details of the internal structure calculations. The value of  $\Delta H^0 = 18$  meV is indicated in the figure. Reprinted from Ref. [26].

of energy levels involved in this calculation, where both rotational, fine structure, and electronic energies are comparable to the reaction endothermicity is shown in Figure 17.

We used the 22-pole trap apparatus combined with the beam source of atomic hydrogen to study the reaction of  $\text{NH}^+$  with H atoms. An example of data obtained with the H atom beam on and off (blocked by a shutter) is shown in Figure 18. The rate coefficient of reaction (25) was extracted by fitting the data with H beam *on* and *off* with a kinetic model that also includes the reaction of  $\text{NH}^+$  with  $\text{H}_2$  in the trap and takes into account the small fraction of  $^{15}\text{N}^+$  that are produced in the ion source.

In this type of experiment, the temperature of the H atoms  $T_{\text{H}}$  is varied independently from the temperature of the ions  $T_{\text{NH}^+}$  and it is not always possible due to technical limitations to study the reaction at true thermal conditions with  $T_{\text{H}} = T_{\text{NH}^+}$ . We, therefore, have to define an effective collisional temperature. The simplest choice is to define a translational temperature  $T_{\text{t}}$  [30] that characterizes the distribution of relative velocities as

$$T_{\text{t}} = \frac{M_{\text{NH}^+} T_{\text{H}} + M_{\text{H}} T_{\text{NH}^+}}{M_{\text{NH}^+} + M_{\text{H}}}, \quad (29)$$

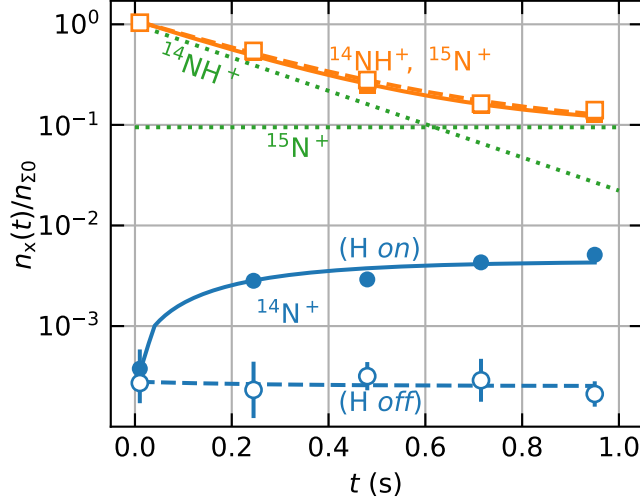


Figure 18: Time evolution of numbers of trapped ions as a function of trapping time, showing the loss of the  $^{14}\text{NH}^+ / ^{15}\text{N}^+$  ions (squares) and formation of the  $\text{N}^+$  ions (circles) in the trap. The curves represent the fits. The measurements were performed with the H beam *on* (closed symbols and solid lines) and H beam *off*, blocked by the shutter (open symbols and dashed lines). The evaluated numbers of  $^{14}\text{NH}^+$  and  $^{15}\text{N}^+$  are indicated by the dotted lines. The measurement was performed at ion and atom temperatures of  $T_{\text{NH}^+} = 26$  K,  $T_{\text{H}} = 75$  K, with H number density of  $n_{\text{H}} = 3.2 \times 10^7 \text{ cm}^{-3}$ . Reprinted from Ref. [26].

where  $M_{\text{NH}^+}$  and  $M_{\text{H}}$  are the  $\text{NH}^+$  and H masses, respectively. To account also for the contribution of the  $\text{NH}^+$  internal energy,  $E_{\text{int}}(T_{\text{NH}^+})$ , to the available collisional energy

$$E_{\text{coll}} = E_{\text{int}}(T_{\text{NH}^+}) + \frac{3}{2}k_{\text{B}}T_{\text{t}}, \quad (30)$$

we can define the corresponding collisional temperature implicitly as the solution of the following formula

$$E_{\text{coll}} = E_{\text{int}}(T_{\text{coll}}) + \frac{3}{2}k_{\text{B}}T_{\text{coll}}. \quad (31)$$

This definition means that thermal reactants at  $T_{\text{coll}}$  would have the same collisional energy as our non-thermal system. The thermal internal energy of  $\text{NH}^+$  is calculated using the energy levels described by the Hamiltonian of Ref. [117] and the equation (31) is solved numerically.

The rate coefficients of reaction (25) obtained as a function of translational and collisional temperatures are shown in the upper panel of Figure 19. For completeness, we also plot the data as a function of the  $\text{NH}^+$  internal temperature  $T_{\text{NH}^+}$ . For calculation of the reaction endothermicity, we also evaluate the thermal rate coefficient of reaction (20) from the measurements with normal and para-enriched  $\text{H}_2$

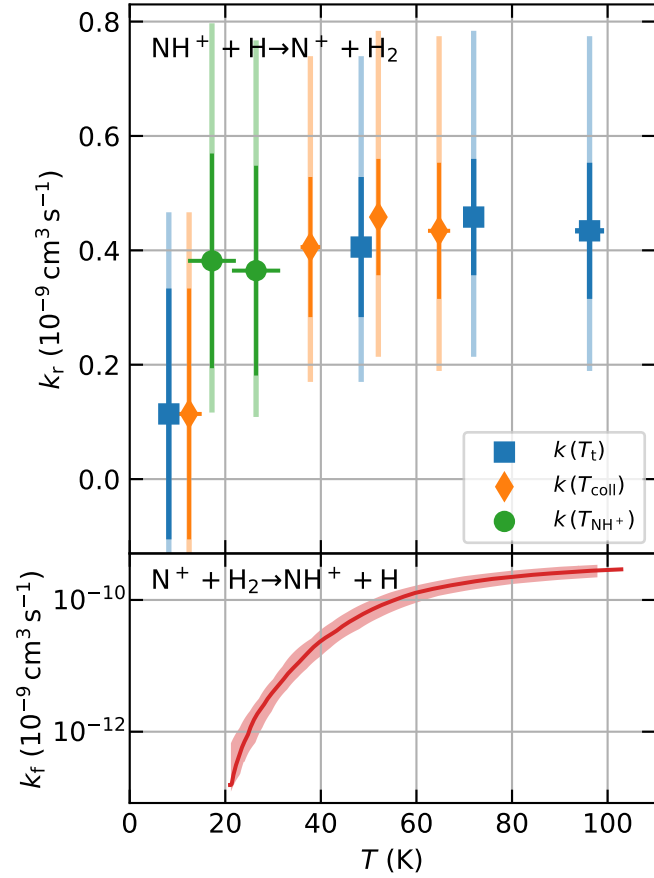


Figure 19: Upper panel—the measured rate coefficients of the reverse reaction as a function of translational, collisional, and  $\text{NH}^+$  internal temperatures. The inner error bars indicate the statistical errors, whereas the outer error bars include also the systematic uncertainty due to  $n_{\text{H}}$  calibration. Lower panel—The rate coefficient of the forward reaction extracted from the data of Ref. [75]. The systematic error of the data is indicated by the filled band. Reprinted from Ref. [26].

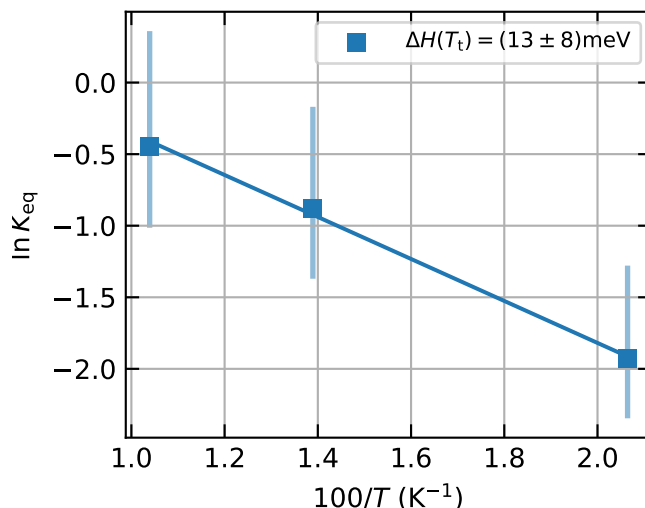


Figure 20: Van 't Hoff plot of  $\ln K_{\text{eq}}$  versus  $100/T$ . For simplicity, only the data as a function of  $T_t$  are presented. The reaction endothermicity obtained from the slope of the linear fit is indicated in the legend.

by assuming the thermal population of nuclear spin states. This rate coefficient is shown in the lower panel of Figure 19.

Since we now have the rate coefficients of the forward and reverse processes, we can immediately estimate the reaction endothermicity using the van 't Hoff plot (see Figure 20) without the need for the detailed balance analysis. Fitting the data in the van 't Hoff plot with the linear relationship  $\ln K_{\text{eq}} = -\Delta H/k_{\text{B}}T + \Delta S/k_{\text{B}}$  leads to  $\Delta H = (13 \pm 8) \text{ meV}$ . This estimate has only limited accuracy as it neglects the temperature dependence of  $\Delta H$  and leaves the reaction entropy  $\Delta S$  as a free parameter, although it can be calculated from the molecular structure data. However, it already tells us that majority of the observed activation energy is indeed caused by reaction endothermicity. We will now proceed to the more accurate detailed balance analysis.

The values of  $\Delta H^0$  evaluated from the data in Figure 19 (in the overlapping temperature range of the forward and reverse reaction rate coefficients) are plotted in Figure 21. As expected, the evaluated data do not depend on temperature. We can conclude from the data, that independently of our assumptions concerning the interaction temperature, the reaction enthalpy can be described as

$$\Delta H^0 = (18 \pm 4) \text{ meV}. \quad (32)$$

This value is practically equal to the activation energies determined in the previous studies (see, e. g., the overviews in Refs. [25, 26]), which means that the barrier height is negligible within our accuracy. The hypothetical barrier height  $E_{\text{b}}$  can be quantified by subtracting the

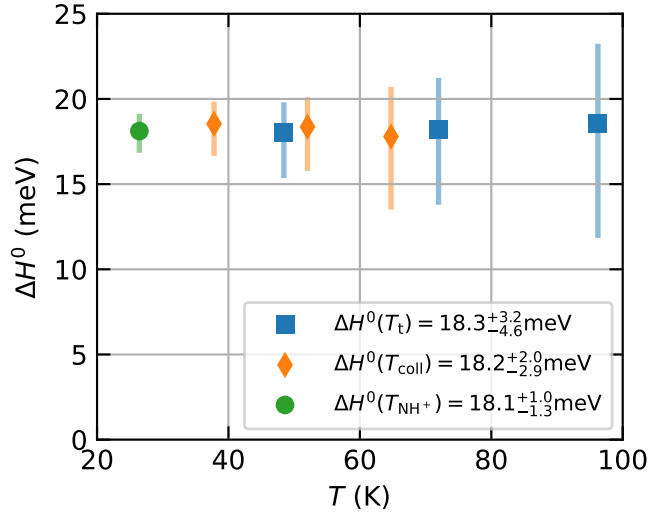


Figure 21: Values of  $\Delta H^0$  of reaction (20) as a function of the translational, collisional, and internal  $\text{NH}^+$  temperatures obtained from the detailed balance principle (28). The overall (systematic + statistical) uncertainties obtained using interval arithmetic from the overall uncertainties of the input data are indicated by the error bars and the weighted mean values are given in the legend. Reprinted from Ref. [26].

endothermicity from the recently determined low-temperature activation energy [25]  $E_A = (19.3 \pm 2.7)$  meV as  $E_b = (2 \pm 5)$  meV.

The known endothermicity of reaction (20) can now be used to provide reliable experimental values of  $\text{NH}^+$  dissociation energies. In particular,  $\Delta H^0$  can be expressed as  $D_0(\text{H}-\text{H}, ^1\Sigma_g) - D_0(\text{N}^+-\text{H}, ^2\Pi)$ , where  $D_0(\text{H}-\text{H}, ^1\Sigma_g)$  and  $D_0(\text{N}^+-\text{H}, ^2\Pi)$  are energies required for dissociation from the  $\text{H}_2(^1\Sigma_g)$  and  $\text{NH}^+(^2\Pi)$  ground states towards the  $\text{H} + \text{H}$  and  $\text{N}^+ + \text{H}$  asymptotes, respectively. Using the value of  $D_0(\text{H}-\text{H}, ^1\Sigma_g) = 4478.1$  meV [118]), we can evaluate

$$D_0(\text{N}^+-\text{H}, ^2\Pi) = D_0(\text{H}-\text{H}, ^1\Sigma_g) - \Delta H^0 = (4460 \pm 4) \text{ meV} \quad (33)$$

in good agreement with the theoretical value of  $D_0(\text{N}^+-\text{H}, ^2\Pi) = 4462$  meV from Ref. [104]. See Ref. [26] for dissociation energies towards other dissociation asymptotes, discussion of electronic transitions, and comparison with other experimental results.

### 3.4 REACTIONS OF $\text{NH}^+$ , $\text{NH}_2^+$ , AND $\text{NH}_3^+$ WITH $\text{H}_2$

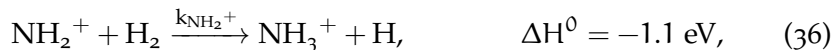
*The results summarized in this section are described in detail by Rednyk et al. [27, Attachment F].*

In the process of ammonia formation in the ISM (19), the weakly endothermic formation of  $\text{NH}^+$  is followed by reaction with  $\text{H}_2$ , which

has two exothermic reaction channels - hydrogen abstraction and proton transfer



and finally, two hydrogen abstraction reactions produce the  $\text{NH}_4^+$  ions



The reactions (34) and (36) are fast with rate coefficients approaching the capture rate coefficients. Previously, these reactions have only been studied at temperatures above 300 K [87, 96, 119] with exception of one study at 15 K [99]. The reaction (34) has also been studied by several recent theoretical studies [120–122].

On the other hand, reaction (37) has a reaction barrier of approximately 0.1 eV and at low temperatures, it can only proceed by tunneling. Owing to its strong temperature dependence and astrophysical importance, this reaction has been studied in a broad range of temperatures in previous experimental studies [96, 99, 123–128]. The reaction has also been studied theoretically, e. g., in Refs. [129, 130].

We studied the reactions (34)–(37) using the 22-pole ion trap in order to provide low-temperature reaction rate coefficients for astrochemical modeling. In principle, the reaction rate coefficients for the whole sequence of hydrogen abstraction reactions (19) can be obtained by just injecting  $\text{N}^+$  into the trap filled with  $\text{H}_2$  and observing the whole chain of reactions at once (see Figure 12). However, since the reactions proceed in the trap at relatively short time scales on the order of milliseconds, the intermediate products don't have enough time to thermalize and we would actually be measuring the reactivity of internally excited ions (see Ref. [27] for discussion and examples of such data). We, therefore, studied each of the reactions (34)–(36) separately by producing the primary reactants in the ion source and injecting them directly into the trap. The exception was reaction (37), which is so slow that the intermediate products ( $\text{NH}_3^+$ ) have enough time to thermalize before a reactive collision occurs.

For brevity, we only present here the results for the  $\text{NH}_2^+ + \text{H}_2$  reaction, as these may have the biggest impact on astrochemical models. The remaining results are presented in Ref. [27] in detail. A sample of primary experimental data is shown in Figure 22 and the resulting temperature dependence of the reaction coefficient of reaction (36) is presented in Figure 23. The large discrepancy with the value of Ref. [99] is caused by internal excitation of  $\text{NH}_2^+$  in Ref. [99], where the rate coefficient was measured by injecting  $\text{N}^+$  into the trap and

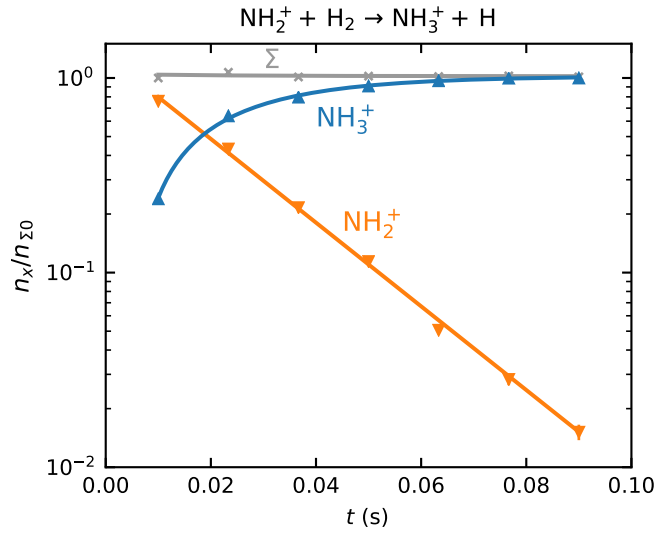


Figure 22: Time evolution of the normalized numbers of  $\text{NH}_2^+$  and  $\text{NH}_3^+$  ions measured at collisional temperature  $T = 39$  K with  $\text{H}_2$  number density  $[\text{H}_2] = 6.2 \times 10^{10} \text{ cm}^{-3}$ . The fitted kinetic model is indicated by the solid curves. The total number of ions ( $\Sigma$ ) is also indicated. Reprinted from Ref. [27].

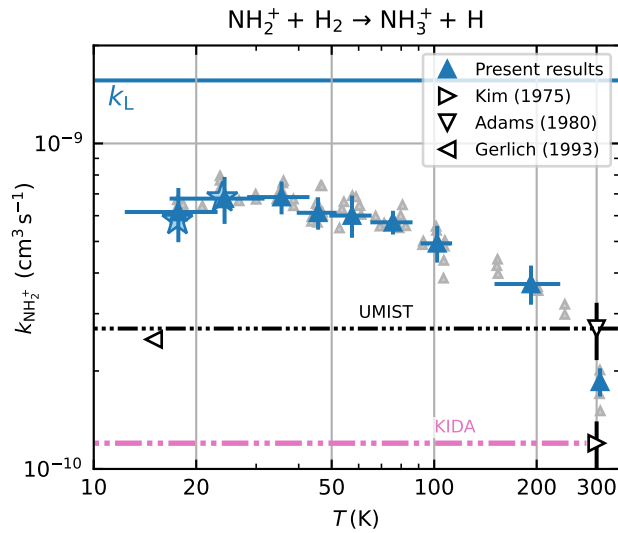


Figure 23: Temperature dependence of the rate coefficient of reaction (36). The present data are compared with previous results of Kim et al. [96], Adams et al. [119], and Gerlich [99]. The low-temperature values used in the UMIST and KIDA databases are also shown for comparison. Adapted from Ref. [27]



observing the whole sequence of hydrogen abstraction reactions at once. We were able to reproduce the value of Ref. [99] when equivalent conditions were used.

Figure 23 shows that the low-temperature rate coefficients of reaction (36) are significantly underestimated in the KIDA [131] and UMIST [60] astrochemistry databases and incorporation of the present values into astrochemical reaction networks should notably improve the accuracy of the calculated nitrogen hydride number densities.



SUMMARY AND OUTLOOK

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This thesis summarizes the results I obtained in collaboration mainly with my colleagues in the group of prof. Glosík at the Charles University, and partly with the group of prof. Wester at the University of Innsbruck. The work was also significantly influenced and motivated by collaboration with prof. Dieter Gerlich. The published papers also contain significant contributions by quantum theorists from the Institute of Theoretical Physics at Charles University.

Despite the decades of previous research in the field of laboratory astrochemistry, the reaction coefficients of most reactions relevant to the chemistry of interstellar clouds are only known at, or above, room temperature (if at all) and only a small fraction of reactions has been studied at relevant temperatures between 10 K and 100 K. This work confirms that ion trapping is a state-of-the-art technique capable of providing unique chemical kinetic data at astrophysically relevant cryogenic temperatures. We have also shown that, in addition to providing rate coefficient for astrochemical models, low-temperature experiments can provide valuable insights into the reaction dynamics and internal structure of molecules. In particular, we have studied the effects of isotopic substitution, rotational excitation of  $\text{H}_2$ , and even isotopic electronic shifts.

As a part of my current research grant, we are now working on further developments in this direction, preparing first absolute measurements of rate coefficients of  $\text{H}_2 + \text{H}_3^+$  rotational state-changing collisions, to better understand the astronomically observed ortho / para ratios, and constructing a source of vibrationally excited  $\text{H}_2$ , to investigate its role in the formations of interstellar carbon hydrides.



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## LIST OF PUBLICATIONS IN IMPACTED JOURNALS

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List of publications in impacted journals (co)authored by the thesis author.

- [1] Š. Roučka, S. Rednyk, T. D. Tran, A. Kovalenko, D. Mulin, S. S. Kumar, P. Dohnal, R. Plašil, and J. Glosík. "Endothermicity of the  $N^+ + H_2 \rightarrow NH^+ + H$  Reaction – Experimental Study of the Reverse Process." In: *Phys. Rev. Lett.* (2022).
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## ATTACHED PUBLICATIONS





ELECTRON TRANSFER AND ASSOCIATIVE  
DETACHMENT IN LOW-TEMPERATURE  
COLLISIONS OF  $D^-$  WITH H

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*Bibliographic record of the attached publication:*

Š. Roučka, D. Mulin, P. Jusko, M. Čížek, J. Eliášek, R. Plašil, D. Gerlich, and J. Glosík. "Electron Transfer and Associative Detachment in Low-Temperature Collisions of  $D^-$  with H." In: *J. Phys. Chem. Lett.* 6.23 (2015), pp. 4762–4766.  
DOI: [10.1021/acs.jpcllett.5b02155](https://doi.org/10.1021/acs.jpcllett.5b02155).

*Attachment not included in this short version of the thesis.*



COMPLEX FORMATION AND INTERNAL  
PROTON-TRANSFER OF HYDROXYL-HYDROGEN  
ANION COMPLEXES AT LOW TEMPERATURE

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*Bibliographic record of the attached publication:*

- D. Hauser, O. Lakhmanskaya, S. Lee, Š. Roučka, and R. Wester. "Complex Formation and Internal Proton-Transfer of Hydroxyl-Hydrogen Anion Complexes at Low Temperature." In: *New J. Phys.* 17.7 (2015), p. 075013.  
DOI: [10.1088/1367-2630/17/7/075013](https://doi.org/10.1088/1367-2630/17/7/075013).

*Attachment not included in this short version of the thesis.*





EFFECT OF ROTATIONAL EXCITATION OF H<sub>2</sub> ON  
ISOTOPIC EXCHANGE REACTION WITH OD<sup>-</sup> AT  
LOW TEMPERATURES

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*Bibliographic record of the attached publication:*

Š. Roučka, S. Rednyk, A. Kovalenko, T. D. Tran, R. Plašil, Á. Kálosi, P. Dohnal, D. Gerlich, and J. Glosík. "Effect of Rotational Excitation of H<sub>2</sub> on Isotopic Exchange Reaction with OD<sup>-</sup> at Low Temperatures." In: *Astron. Astrophys.* 615 (2018), p. L6.  
DOI: [10.1051/0004-6361/201833264](https://doi.org/10.1051/0004-6361/201833264).

*Attachment not included in this short version of the thesis.*



FORMATION OF  $\text{H}_2\text{O}^+$  AND  $\text{H}_3\text{O}^+$  CATIONS IN  
REACTIONS OF  $\text{OH}^+$  AND  $\text{H}_2\text{O}^+$  WITH  $\text{H}_2$  :  
EXPERIMENTAL STUDIES OF THE REACTION RATE  
COEFFICIENTS FROM  $T = 15$  TO  $300$  K

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*Bibliographic record of the attached publication:*

- T. D. Tran, S. Rednyk, A. Kovalenko, Š. Roučka, P. Dohnal, R. Plašil, Dieter Gerlich, and J. Glošík. "Formation of  $\text{H}_2\text{O}^+$  and  $\text{H}_3\text{O}^+$  Cations in Reactions of  $\text{OH}^+$  and  $\text{H}_2\text{O}^+$  with  $\text{H}_2$  : Experimental Studies of the Reaction Rate Coefficients from  $T = 15$  to  $300$  K." In: *Astrophys. J.* 854.1 (2018), p. 25.  
DOI: [10.3847/1538-4357/aaa0d8](https://doi.org/10.3847/1538-4357/aaa0d8).

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OH<sup>+</sup> FORMATION IN THE LOW-TEMPERATURE  
O<sup>+</sup> (4S) + H<sub>2</sub> REACTION

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*Bibliographic record of the attached publication:*

- A. Kovalenko, T. D. Tran, S. Rednyk, Š. Roučka, P. Dohnal, R. Plašil, Dieter Gerlich, and J. Glosík. "OH<sup>+</sup> Formation in the Low-Temperature O<sup>+</sup>(4 S) + H<sub>2</sub> Reaction." In: *Astrophys. J.* 856.2 (2018), p. 100.  
DOI: [10.3847/1538-4357/aab106](https://doi.org/10.3847/1538-4357/aab106).

*Attachment not included in this short version of the thesis.*



REACTION OF  $\text{NH}^+$ ,  $\text{NH}_2^+$ , AND  $\text{NH}_3^+$  IONS WITH  $\text{H}_2$  AT LOW TEMPERATURES: THE PATHWAY TO AMMONIA PRODUCTION IN THE INTERSTELLAR MEDIUM

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*Bibliographic record of the attached publication:*

- S. Rednyk, Š. Roučka, A. Kovalenko, T. D. Tran, P. Dohnal, R. Plašil, and J. Glosík. "Reaction of  $\text{NH}^+$ ,  $\text{NH}_2^+$ , and  $\text{NH}_3^+$  Ions with  $\text{H}_2$  at Low Temperatures: The Pathway to Ammonia Production in the Interstellar Medium." In: *Astron. Astrophys.* 625 (2019), A74.  
DOI: [10.1051/0004-6361/201834149](https://doi.org/10.1051/0004-6361/201834149).

*Attachment not included in this short version of the thesis.*





THE REACTION OF O<sup>+</sup> (4S) IONS WITH H<sub>2</sub>, HD,  
AND D<sub>2</sub> AT LOW TEMPERATURES: EXPERIMENTAL  
STUDY OF THE ISOTOPE EFFECT

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*Bibliographic record of the attached publication:*

A. Kovalenko, Š. Roučka, T. D. Tran, S. Rednyk, R. Plašil, P. Dohnal,  
and J. Glosík. "The Reaction of O<sup>+</sup>(4 S) Ions with H<sub>2</sub>, HD, and D<sub>2</sub>  
at Low Temperatures: Experimental Study of the Isotope Effect."  
In: *J. Chem. Phys.* 154.9 (2021), p. 094301.  
DOI: [10.1063/5.0036049](https://doi.org/10.1063/5.0036049).

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REACTION OF  $N^+$  ION WITH  $H_2$ , HD, AND  $D_2$  AT  
LOW TEMPERATURES: EXPERIMENTAL STUDY OF  
THE PATHWAY TO DEUTERATED  
NITROGEN-CONTAINING MOLECULES IN THE  
INTERSTELLAR MEDIUM.

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*Bibliographic record of the attached publication:*

- R. Plašil, Š. Roučka, A. Kovalenko, T. D. Tran, S. Rednyk, P. Dohnal, D. Shapko, D. Gerlich, and J. Glosík. "Reaction of  $N^+$  Ion with  $H_2$ , HD, and  $D_2$  at Low Temperatures: Experimental Study of the Pathway to Deuterated Nitrogen-Containing Molecules in the Interstellar Medium." In: *Submitted to Astrophys. J.* (2021).

*Attachment not included in this short version of the thesis.*



ENDOTHERMICITY OF THE  $N^+ + H_2 \rightarrow NH^+ + H$   
REACTION — EXPERIMENTAL STUDY OF THE  
REVERSE PROCESS

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*Bibliographic record of the attached publication:*

Š. Roučka, S. Rednyk, T. D. Tran, A. Kovalenko, D. Mulin, S. S. Kumar, P. Dohnal, R. Plašil, and J. Glosík. "Endothermicity of the  $N^+ + H_2 \rightarrow NH^+ + H$  Reaction – Experimental Study of the Reverse Process." In: *In Preparation for: Phys. Rev. Lett.* (2022).

*Attachment not included in this short version of the thesis.*