Penning Ionization of N_2 by Helium Metastable Atoms

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Abstract. Study of Penning ionization was performed on Cryogenic stationary afterglow apparatus with Cavity Ring Down Spectroscopy in connection with measurement of N_2^+ recombination. Based on the evolution of the number densities of electrons and N_2^+, we have determined the rate coefficients of the reaction of N_2 with helium metastable atoms in the afterglow under certain conditions.

Introduction

Penning ionization is an important atomic collision process, in which ions are produced in a chemical reactions with excited atoms. The excited atoms are metastable due to their long lifetime. Collision of such excited atom with another atom or molecule results in ionization of the latter atom or molecule:

$$He^* + M \rightarrow He + M^+ + e^- \tag{1}$$

where M denotes an atom or a molecule.

Penning ionization is a fast process that affects the characterization of electrical discharges and thermal plasmas [*Siska*, 1993] and is also important for atmospheric chemistry of planets, including Earth [*Biondini et al.*, 2005]. Given the composition of planetary atmospheres, gas atoms can be involved in several phenomena on Earth and other planets in the Solar System, like Mercury or Mars [*Alagia et al.*, 2013].

Penning ionization has many applications, such as surface characterization studies [*Harada et al.*, 1997] or mass spectroscopy [*Cody et al.*, 2005]. Penning ionization is a phenomenon where discrete states are immersed within a continuous range of states and these are interconnected and influenced by each other, resulting in an autoionization process [*Miller*, 2003], although only through collision can the autoionization collision complex be formed. Nuclear dynamics play an important role in Penning ionization reactions. Part of the previous experiment performed by *Margulis et al.* [2020] was ionization induced by collision of the excited noble gas and a neutral particle. This initiates dynamics between ions and noble gas atoms, which could lead to quantum state-to-state resolution [*Margulis et al.*, 2020]. Other experiments studying the dynamics used different methods, such as cross beam [*Mikosch et al.*, 2008; *Stei et al.*, 2015], collisions within the orbit of the Rydberg electron [*Allmendinger et al.*, 2016b,a] or the co-trapping of ions and atoms [*Hall and Willitsch*, 2012].

There are more options for an observation of the molecular dynamics than collision. If a molecule gets excited into a nonstationary state, a dynamical information can be obtained from a time-resolved spectroscopy of dissociation fragments [*Zewail*, 2000].

In low temperature afterglow plasma such as in present experiments, the helium metastable atoms collide with electrons in superelastic collisions. The helium metastable is deexcited and the electron gains energy of around 20 eV [*Alagia et al.*, 2013]. Such amount of energy is the source of electron heating, which is often undesirable, especially in recombination studies. It can be prevented by utilizing Penning ionization. In our case the molecule reacting with helium metastable atoms was N_2 and therefore the creation of the warm electrons can be prevented. Previous studies on Penning ionization of N_2 in collisions with helium metastable atoms were performed for temperatures of 300 K [*Lindinger et al.*, 1974] or higher and our goal was to determine if the metastable atoms are also effectively eliminated in the temperature range covered by our recent study of N_2^+ recombination with electrons [*Uvarova et al.*, 2023].

There have been recent studies on Penning ionization of metastable helium (or neon) with molecular hydrogen (or HD) in cold beams, where sharp scattering resonances were observed at low temperatures [*Henson et al.*, 2012; *Klein et al.*, 2017; *Margulis et al.*, 2020].

Experiment

The experiment was performed using Cryogenic Stationary afterglow apparatus with Cavity Ring Down Spectrometer (Cryo-SA-CRDS). A simplified scheme is in Figure 1. Detailed description can be found in [*Plašil et al.*, 2018; *Shapko et al.*, 2021].

Gas of the required composition enters the discharge tube on one side and is pumped by a roots pump on the other side. The plasma is produced in a sapphire discharge tube (blue in the picture) by a microwave discharge in a prepared gas mixture. The discharge tube is connected by copper braids to a microwave resonator. It is cooled by a coldhead and the whole setup is vacuum insulated. There are several temperature sensors inside and the dashed line shows the optical axis between the highly reflective mirrors, as seen in Figure 1.

The optical cavity consists of two highly reflective plano-concave mirrors with a reflectivity greater than 99.99%. Radius of curvature is 1 m and the distance of the mirrors is 80 cm. The light that leaves the cavity through the mirror is then detected by the detector consisting of an avallanche photodiode with an amplifier. For the experiment with N_2^+ ions we used optical system consisting of two lasers (L785P090 with central wavelength of 785 nm and L808P030 centered at 808 nm). For the measurement itself, we have only used laser with wavelenght of 785 nm. Laser with wavelenght of 808 nm was used to observe vibrationally excited N_2^+, which has given us an advantage compared to previous experiments. We were able to confirm [*Uvarova et al.*, 2023] that the amount of hot vibrationally excited ions is very low — around 1.5 %. Based on the measurement, we were also able to confirm that the rotational temperature of the ions was close to the temperature measured at the discharge tube holder. Transitions covered in this experiment were in Meinel band of N_2^+ $^2\Sigma_g^+$ — $^2\Pi_u$ originating in the ground and the first vibrational state of the ion. For spectroscopic notation see *Wu et al.* [2007].

Both lasers were on a separate optical bench and were coupled to a single fiber. Doing so, we have ensured that even though the lasers were free spaced, as soon as they are coupled into a single mode fiber, we get the same profile. Therefore, both lasers had the same profile and were positioned on the same optical path. For details see *Uvarova et al.* [2023].

Results and discussion

Prior to the measurement of Penning ionization, we have used a model of chemical kinetics [*Uvarova et al.*, 2023]. The model was used to find ideal conditions for our experiment. Kinetic model consists of several reactions, which we can see in Table 1 and is too complicated for the fitting procedure, therefore we only chose the most important reactions that are the most influential while determining the Penning ionization rate coefficient. We have selected the most important equations for early afterglow and therefore we have minimized the whole system to make the fitting procedure easier. We have used these differential equations (2), and then fitted them directly to the measured time evolutions of N_2^+ and electron number densities:

$$\begin{aligned}
\frac{\partial[e^-]}{\partial t} &= -\alpha_{N_2^+}[N_2^+][e^-] - \alpha_{N_4^+}[N_4^+][e^-] + k_p[N_2][He^*] \\
\frac{\partial[N_2^+]}{\partial t} &= k_p[N_2][He^*] - \alpha_{N_2^+}[N_2^+][e^-] - k_f[N_2][He][N_2^+] \\
\frac{\partial[N_4^+]}{\partial t} &= k_f[N_2][He][N_2^+] - \alpha_{N_4^+}[N_4^+][e^-] \\
\frac{\partial[He^m]}{\partial t} &= -k_p[N_2][He^*]
\end{aligned} \tag{2}$$

The differential equations are based on gain and loss of the given particle, based on reactions R8, R10, and R12 from the Table 1 and the Penning ionization k_P, which is the subject of this study. $\alpha_{N_2^+}$ and $\alpha_{N_4^+}$ are recombination coefficients for $[N_2^+]$ and $[N_4^+]$ respectively and k_f is the 3-particle association constant. We did not consider R9, as it does not have a great effect on plasma decay in the reactions. Given the time scale, which we were observing, the characteristic reaction time of R9 is too large.

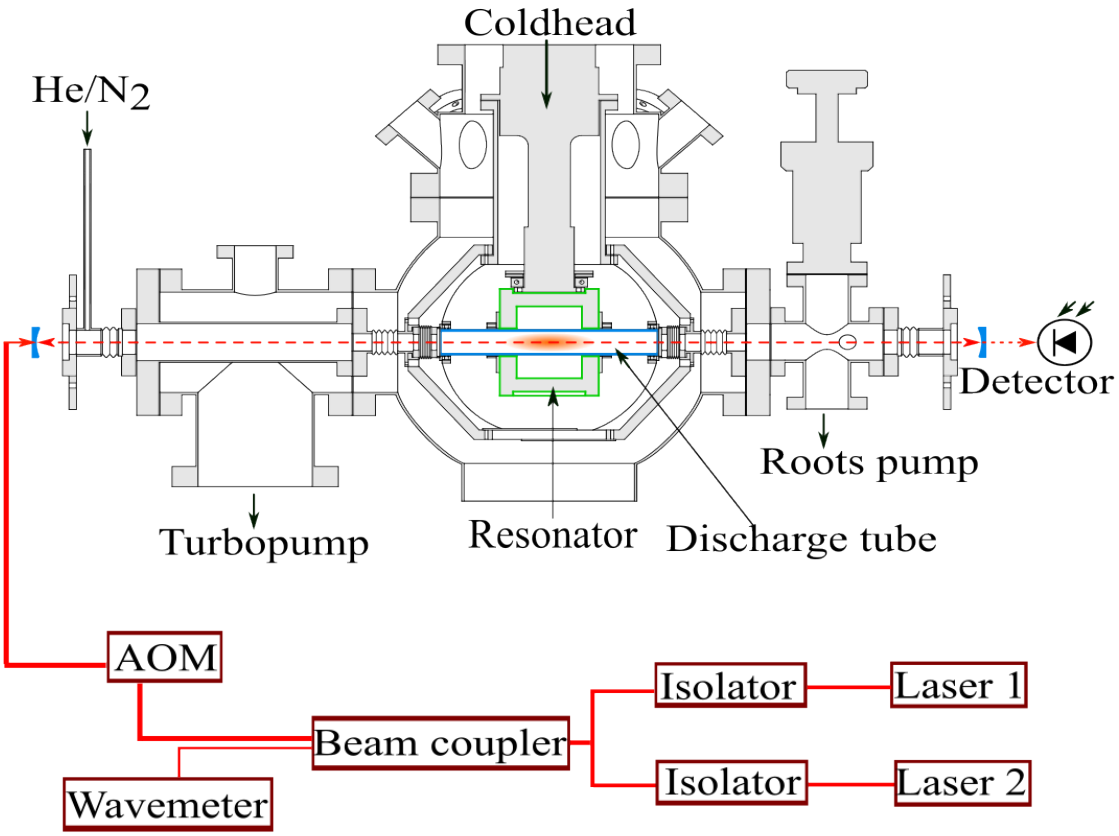

Figure 1. A scheme of CRYO-SA-CRDS. The discharge tube is depicted in blue frame. The microwave resonator is around the tube and is shown in green. The Sumitomo RDK 408S cold head is located above the microwave resonator and it enables temperature range of 30–300 K. The laser light is controlled by an acousto–optic modulator (AOM) and passes through the first mirror, the discharge tube and the second mirror on the other side of the discharge tube and then to the detector.

Table 1. The most important reactions for formation and destruction of N_2^+ ions included in the model of chemical kinetics. The characteristic reaction times were calculated using the formula: $\tau = 1/k[R]$, where k is the rate coefficient of the reaction, $[R]$ is the neutral reactant number density for the two body reactions and the product of the neutral reactant number densities for the three body reactions. The number densities used in the model were [He] = 8.9×10^{16} cm^{-3} and [N_2] = 2.4×10^{14} cm^{-3}.

No.	Reaction	Rate coefficient $[cm^3s^{-1}]$, $[cm^6s^{-1}]$	Characteristic reaction time $[s]$	Reference
R1	$He^* + N_2 \rightarrow N_2^+ + He + e^-$	6.1×10^{-11}	6.83×10^{-5}	[*Lindinger et al.*, 1974]
R2	$He^+ + He + He \rightarrow He_2^+ + He$	1.0×10^{-31}	1.26×10^{-3}	[*Glosik et al.*, 2015]
R3	$He_2^+ + N_2 \rightarrow N_2^+ + He + He$	1.12×10^{-9}	3.72×10^{-6}	[*Lindinger et al.*, 1974]
R4	$N^+ + N_2 + He \rightarrow N_3^+ + He$	4.0×10^{-29}	1.17×10^{-3}	[*Anicich et al.*, 2000]
R5	$N^+ + N_2 + N_2 \rightarrow N_3^+ + N_2$	8.6×10^{-30}	2.02×10^{0}	[*Anicich et al.*, 2000]
R6	$He^+ + N_2 \rightarrow N^+ + He + N$	8.4×10^{-10}	4.96×10^{-6}	[*Lane*, 1986]
R7	$He^+ + N_2 \rightarrow N_2^+ + He$	6.6×10^{-10}	6.31×10^{-6}	[*Lane*, 1986]
R8	$N_2^+ + N_2 + He \rightarrow N_4^+ + He$	1.9×10^{-29}	2.46×10^{-3}	[*Anicich et al.*, 2000]
R9	$N_2^+ + N_2 + N_2 \rightarrow N_4^+ + N_2$	8.0×10^{-29}	2.17×10^{-1}	[*Anicich et al.*, 2000]
R10	$N_2^+ + e^- \rightarrow N + N$	3.5×10^{-7}	1.90×10^{-4}	Present data
R11	$N_3^+ + e^- \rightarrow N_2 + N$	6.5×10^{-7}	1.03×10^{-4}	[*Zhaunerchyk et al.*, 2007]
R12	$N_4^+ + e^- \rightarrow N_2 + N_2$	2.6×10^{-6}	2.56×10^{-5}	[*Adams et al.*, 2009]

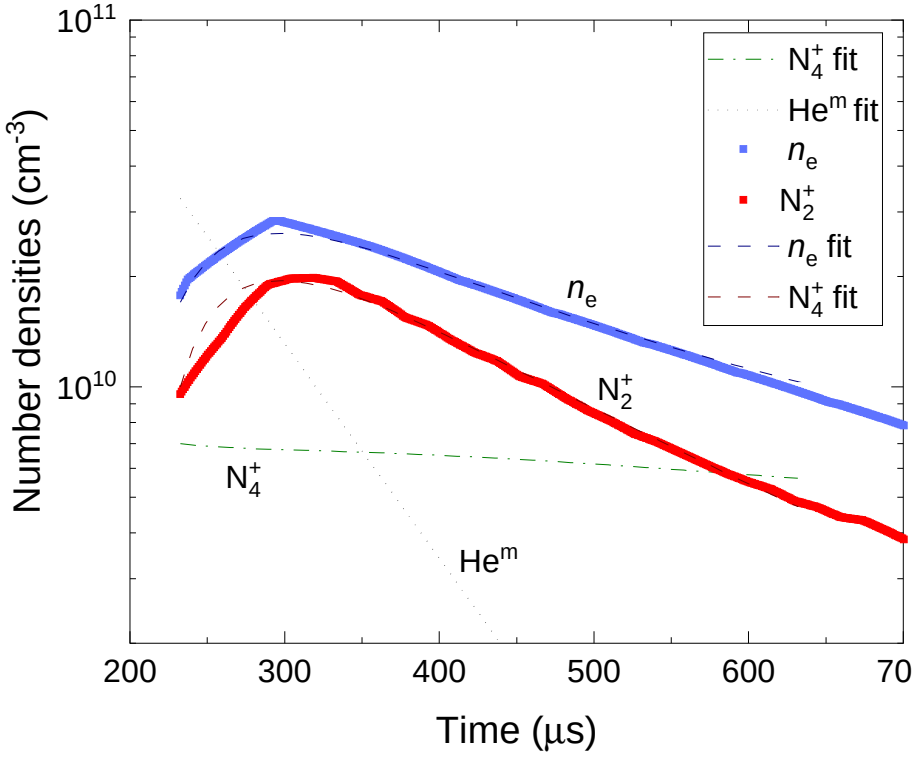

Figure 2. The time evolution of the measured number densities (thick lines) and the number densities obtained from the kinetic model. Blue and red squares denote the number densities of electrons and N_2^+ respectively, obtained from the fit. The blue and red dashed lines denote the fit of the number densities of electrons and N_2^+ respectively. Green dot-dashed line denotes the fit of N_4^+ and the black dotted line denotes the fit of He^*. The temperature for both the measured data and the data obtained from kinetic model was T = 200 K. The number densities used in the model were [He] = 8.9×10^{16} cm^{-3} and [N_2] = 2.4×10^{14} cm^{-3}.

The fitting procedure was done by taking a set of data from the experiment, consisting of a time evolution of the number densities of electrons and N_2^+. Based on the differential equations (2), we were also able to predict the time evolution of He^* and N_4^+ as is depicted in Graph (2).

We have a different time step for measurement of both the number density of electrons and the number density of ions. For fitting, it is necessary for the fitting procedure to have the same time step. Therefore we use linear interpolation of the electron number density. This approach is not entirely correct, however the error created this way is small.

We presume that the main loss process of N_2^+ ions in the early afterglow in our experiment is the recombination. We do not know the temperature of the electrons and in case this temperature is high, another loss process — ambipolar diffusion — could play a role. Based on experiments in FALP (Flowing Afterglow Langmuir Probe) [*Korolov et al.*, 2008] conducted at similar conditions as in present studies, the electron temperature in afterglow plasma containing metastable helium atoms can be in hundreds of Kelvin, but should not substantially exceed a thousand Kelvins. Although we acknowledge the inherent flaw in our assumption, it remains our most accurate estimation.

Based on the fitting procedure from data shown in Figure 2, we have determined the Penning ionization rate coefficient $k_\mathrm{p} = (5.72 \pm 0.98) \times 10^{-11}\mathrm{cm}^3\mathrm{s}^{-1}$ at 200 K, which is in good agreement with the previous experiment by *Lindinger et al.* [1974].

Figure 3 shows the measurement of the Penning ionization rate coefficient k_P in 200 K and was compared to the data fit from [*Lindinger et al.*, 1974]. The error bar shown in Figure 3 is a statistical

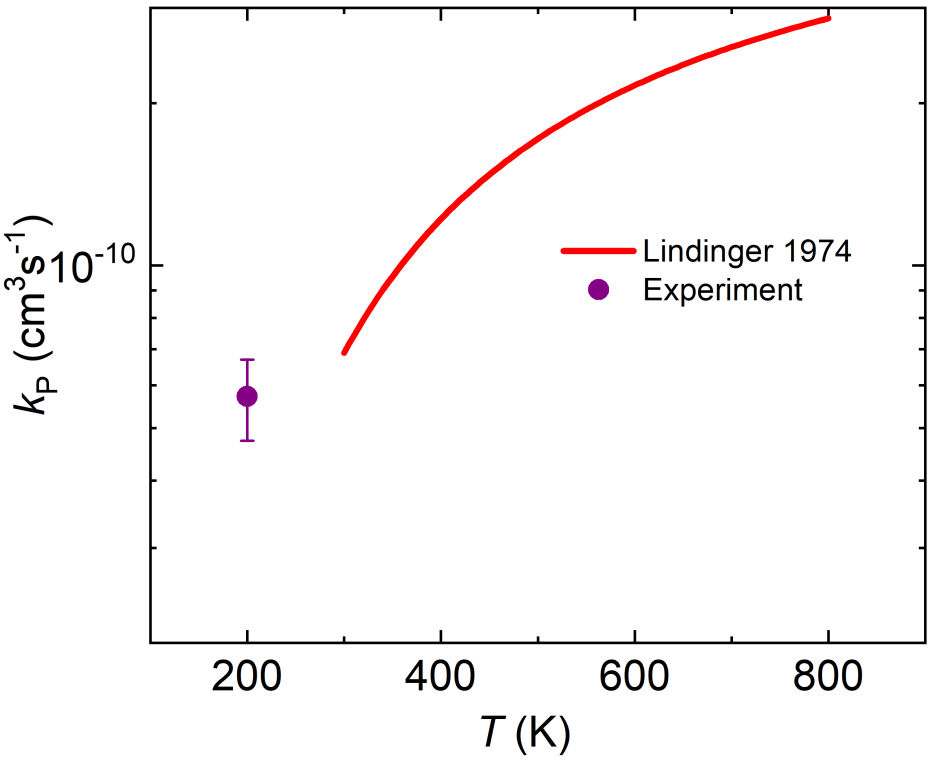

Figure 3. The temperature dependence of the Penning ionization rate coefficient k_P for the reaction He^* + N_2. The value of k_P was obtained from the increase of the electron and N_2^+ number densities in the early afterglow plasma. The full line denotes fit of values of k_P measured by *Lindinger et al.* [1974].

error, given by error of the fit, which is around 20 %. The cause of such high statistical error is the fact that we are fitting a set of differential equations (2). The estimated systematic error is 100 %, meaning the obtained k_P could be two times higher or lower. The main problem is, we do not know the loss term for N_2^+ ions in the differential equations (2). If we change the main loss process to ambipolar diffusion, in case of warm electrons, the value of k_P could be different.

Conclusion

We have studied the Penning ionisation of N_2 in collisions with helium metastable atoms in 200 K. The obtained reaction rate coefficient is shown in Figure 3 and is in good agreement with previous studies performed at higher temperatures [*Lindinger et al.*, 1974]. The obtained Penning ionization rate coefficient $k_p = (5.72 \pm 0.98) \times 10^{-11} \mathrm{cm}^3\mathrm{s}^{-1}$. These results show that under conditions from *Uvarova et al.* [2023], metastable atoms are quickly removed from the afterglow plasma.

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