A study of the translational temperature dependence of the reaction rate constant between CH$_3$CN and Ne$^+$ at low temperatures

Cite as: J. Chem. Phys. 153, 124305 (2020); https://doi.org/10.1063/5.0013807
Submitted: 14 May 2020. Accepted: 10 September 2020. Published Online: 30 September 2020

Kunihiro Okada, Kazuhiro Sakimoto, Yusuke Takada, and Hans A. Schuessler

ARTICLES YOU MAY BE INTERESTED IN

Reactions of translationally cold trapped CCl$^+$ with acetylene (C$_2$H$_2$)
The Journal of Chemical Physics 152, 234310 (2020); https://doi.org/10.1063/5.0008656

Threshold photoelectron spectroscopy of the HO$_2$ radical
The Journal of Chemical Physics 153, 124306 (2020); https://doi.org/10.1063/5.0022410

A stand-alone magnetic guide for producing tuneable radical beams
The Journal of Chemical Physics 153, 104202 (2020); https://doi.org/10.1063/5.0020628

Your Qubits. Measured.
Meet the next generation of quantum analyzers

- Readout for up to 64 qubits
- Operation at up to 8.5 GHz, mixer-calibration-free
- Signal optimization with minimal latency

Find out more

AIP Publishing

© 2020 Author(s).
A study of the translational temperature dependence of the reaction rate constant between CH$_3$CN and Ne$^+$ at low temperatures

Cite as: J. Chem. Phys. 153, 124305 (2020); doi: 10.1063/5.0013807
Submitted: 14 May 2020 • Accepted: 10 September 2020 • Published Online: 30 September 2020

Kunihiro Okada, Kazuhiro Sakimoto, Yusuke Takada, and Hans A. Schuessler

AFFILIATIONS
1 Department of Physics, Sophia University, 7-1 Kioicho, Chiyoda, Tokyo 102-8554, Japan
2 Department of Physics and Astronomy, Texas A&M University, College Station, Texas 77843-4242, USA

ABSTRACT
We have measured the translational temperature dependence of the reaction rate constant for CH$_3$CN + Ne$^+$ → products at low temperatures. A cold Ne$^+$ ensemble was embedded in Ca$^+$ Coulomb crystals by a sympathetic laser cooling technique, while cold acetonitrile (CH$_3$CN) molecules were produced by two types of Stark velocity filters to widely change the translational temperatures. The measured reaction rate constant gradually increases with the decrease in the translational temperature of the velocity-selected CH$_3$CN molecules from 60 K down to 2 K, and thereby, a steep increase was observed at temperatures lower than 5 K. A comparison between experimental rate constants and the ion–dipole capture rate constants by the Perturbed Rotational State (PRS) theory was performed. The PRS capture rate constant reproduces well the reaction rate constant at a few kelvin but not for temperatures higher than 5 K. The result indicates that the reaction probability is small compared to typical ion–polar molecule reactions at temperatures above 5 K.

Published under license by AIP Publishing. https://doi.org/10.1063/5.0013807

I. INTRODUCTION
Modern astronomical observatories, such as at the Atacama Large Millimeter/submillimeter Array (ALMA), enable us to observe with high spatial resolution the details of chemical compositions and their distribution in interstellar clouds and protoplanetary disks. Recently, many astronomical observations urge astrochemists to update the existing astrochemical models of these celestial bodies. For this purpose, further detailed information about gas-phase (also grain-surface) chemical processes is necessary to be acquired. In the gas-phase processes, the information on the reaction temperature dependence and branching ratios of ion–molecule reactions is in high demand since ion–molecule reactions play important roles in interstellar chemistry.

In general, the ion–molecule reactions at low temperatures are well described by the Langevin model in which the rate constants are independent of the reaction temperatures. The temperature dependence of the rate constants in ion–polar molecule reactions is considered based on the classical ion–dipole capture models. These simple classical models give only capture-rate constants but not reaction branching ratios and are not necessarily sufficient for considering the chemical composition of relatively active interstellar matter such as falling gas forming a disk around a protostar.

Many astrochemical relevant measurements of ion–molecule reactions have been performed so far using various experimental techniques, and some important findings were obtained. For instance, deuteration fractionation and isomerization of molecules are important information to know physical and chemical conditions of interstellar clouds. More accurate temperature dependences of the reaction rate constants are also necessary to refine the reaction networks in interstellar chemical models. Interestingly, strong temperature dependences of the reaction rate constants in NH$_3$ + H$_2$ → NH$_4^+$ + H and C$_3$H$_n^+$ + H$_2$ (n = 0, 1) were found at low temperatures. The former slow reaction is known to be key to the gas-phase ammonia synthesis in interstellar space and has been extensively studied experimentally and theoretically.
Despite the above vigorous past studies, the obtained knowledge is still insufficient to describe the chemical compositions of interstellar matter obtained by state-of-the-art observatories. Most of the previous measurements were performed for restricted ion–molecule reactions and in the limited temperature range near room temperature.\textsuperscript{2,3} Particularly, reaction rate measurements between an ion and polar molecule have not been extensively performed using drift tube methods and cryogenic multipole ion traps at low temperatures because a polar molecular beam is very hard to focus and control. Therefore, there is a wide demand for detailed low-temperature measurements.

Recent experimental developments combining a linear Paul trap (LPT) for the generation of Coulomb crystals with a Stark velocity filter\textsuperscript{4} and a Stark decelera\textsuperscript{4} for producing cold polar molecules enabled us to measure cold ion–polar molecule reactions at low temperatures under ultra-high vacuum conditions.\textsuperscript{1,3,5} We have also demonstrated reaction-rate measurements between sympathetically cooled $\text{N}_2\text{H}^+$ and Ne$^+$ ions and velocity-selected CH$_3$CN molecules,\textsuperscript{5} where CH$_3$CN is known to be one of the important interstellar molecules detected in a protoplanetary disk.\textsuperscript{7} Since one of the important purposes of the present study is to specify the effect of the molecular rotation on the ion–polar molecule reaction, the rotationless atomic form is appropriate as the ions. The existence of the Ne$^+$ ion has been confirmed by x-ray absorption in the interstellar medium,\textsuperscript{6} and the Ne$^+$ reaction could be important in a future model of interstellar chemistry.

Although only the translational temperatures of polar molecules are cold in the above measurements, this general technique has a potential to enable a systematic study of cold ion–polar molecule reactions by changing both the translational and rotational temperatures at the same time by combining the above experimental technique with a buffer-gas cooled molecular source.\textsuperscript{7–9} In this context, we have developed a temperature variable wavy Stark velocity filter\textsuperscript{10} by which we can generate a slow polar molecular beam at translational temperatures from a few to a 100 K. Combining a cryogenic gas cell with the wavy Stark velocity filter enables us to generate slow polar molecules with cold rotational temperatures.

In this paper, we report the measurement of the translational temperature dependence of the reaction rate constant in CH$_3$CN + Ne$^+$ \rightarrow products at low temperatures by combining a sympathetic laser cooling technique with the Stark velocity filter. The results were compared to capture rate constants of the collisions between a polar molecule and an ion. The capture rate constants were evaluated by using perturbed rotational state (PRS) theory\textsuperscript{11,12} in which an adiabatic approximation is introduced for describing the molecular rotation during the collision. The PRS approach was found to be very useful for investigating the rotational excitation of polar molecules by low-energy ion impacts\textsuperscript{13–15} and for understanding the significance of the dipole interaction in the ion–molecule chemical reaction.\textsuperscript{12,14,15} The idea based on the adiabatic approximation was afterward applied to various ion–molecule systems by a lot of workers.\textsuperscript{16–19}

This paper is organized as follows: In Sec. II, we describe our setup and the measurement method of the reaction rate constants. Specifically, the structure and characteristics of the wavy Stark velocity filter combined with a cryogenic linear Paul trap apparatus are presented. We also present a summary of the characterization of the velocity-selected CH$_3$CN molecules generated from two types of Stark velocity filters. A short description of how the average kinetic energy of sympathetically cooled Ne$^+$ ions is evaluated is also presented. In Sec. III, we outline the PRS theory and show some examples of calculated ion–dipole capture cross sections. The procedure to calculate the state-specific PRS capture rate constants is given. Then, we describe how to derive the rotational state distribution of CH$_3$CN from Monte–Carlo trajectory calculations of the velocity-selected CH$_3$CN and how the PRS ion–dipole capture rate constants are obtained from the state-specific rate constants. Next, in Sec. IV, we present the experimental results of the reaction rate measurements and discuss the comparison between the experimental rate constants with the PRS theory. In Sec. V, we further discuss the relation of our study to astrochemistry. Finally, in Sec. VI, we conclude our results and present an outlook for future experiments.

II. EXPERIMENTAL

A. Apparatus

We use two types of Stark velocity filter for producing slow CH$_3$CN molecules in order to cover the wide translational temperature range. One is a standard type Stark velocity filter with a 90$^\circ$ deflection section, which can provide a cold CH$_3$CN beam at a few kelvin. The details of the combined standard Stark velocity filter–ion trap apparatus are described in a previous paper.\textsuperscript{24} The other filter is a wavy Stark velocity filter, which has a wavy deflection section and allows selection of slightly higher translational temperature molecules over a wide range of temperatures in the tens of kelvin range. The detailed description of the wavy Stark velocity filter has also been given previously.\textsuperscript{25}

Here, we briefly describe a combined wavy Stark velocity filter–ion trap apparatus. The schematic of the setup is shown in Fig. 1. A gas reservoir of CH$_3$CN is connected to a gas cell via a Teflon tube with an inner diameter of 2 mm, while the gas cell has an exit aperture with the diameter of 1.5 mm. The exit aperture is positioned closely at the input of the wavy Stark velocity filter. The absolute pressure of CH$_3$CN is typically set to 4.8 Pa, which is monitored at the reservoir by a capacitance manometer (PFEIFFER CMR 364). As the gas cell is thermally contacted to a cryocooler (ULVAC S030), we can cool the gas cell down to 30 K if necessary. The temperature of the cell is monitored by a silicon-diode sensor. The vacuum chamber containing the gas cell is always kept at a lower pressure than $1 \times 10^{-5}$ Pa during the experiment to avoid the loss of slow molecules due to elastic collisions with residual gas molecules.

The extracted polar molecules from the gas cell are guided by the wavy Stark velocity filter, which has a wavy deflection section with a large curvature radius of $R = 1000$ mm and a deflection angle of $\theta = 5^\circ$. A lower left photograph in Fig. 1 shows the wavy deflection section, which is enclosed in a stainless-steel chamber with a dimension of $355 \times 667 \times 300$ mm$^3$. The pressure of the chamber is of the order of $10^{-6}$ Pa during the experiment. The molecular beam guide of the velocity filter consists of four stainless steel rods with a diameter of 2 mm and the distance between the adjacent rods is designed to be 1 mm. The maximum guide...
voltages applied to the quadrupole electrodes is ±2.0 kV, which corresponds to the nominal electric field of 40 kV/cm. Implementing three stages of differential pumping in the wavy Stark velocity filter, we achieve the ultra-high vacuum of $1.5 \times 10^{-8}$ Pa in the ion trap chamber.

The lower right photograph in Fig. 1 shows a cryogenic Linear Paul Trap (LPT) enclosed in double radiation shields, which are thermally contacted to a cryocooler (Iwatani D510, 10 K). As shown in the photograph, we equipped the setup with an electron gun and electron optics for producing Ne$^+$ ions by electron impact ionization. The LPT consists of beryllium copper rods with a diameter of 8 mm and the inner radius $r_0$ of the quadrupole is 3.5 mm. The distance between the end plate electrodes is 10 mm and the static voltages $V_z$ of a few volts are applied to both end electrodes. The LPT is driven by a commercially available radio frequency generator (Stahl-Electronics HF-DR 4.5-900 FL). The driving frequency and the amplitude in balance mode are typically 3.47 MHz and 52 V, respectively. In this case, the radial pseudopotential for Ca$^+$ (Ne$^+$) is 1.1(2.2) eV. Because the base copper plate of the LPT and the electron gun is cooled down to be about 13 K during measurement, we can avoid undesirable reactions between cold ions and stray polar molecules, which are possibly leaked from the area upstream of the wavy Stark velocity filter.

To study the translational reaction temperature dependence of the reaction rate constant between CH$_3$CN and Ne$^+$, we have to characterize the velocity-selected CH$_3$CN at the position of the ion trap. Therefore, we have determined the number density of the velocity-selected CH$_3$CN by the correlation measurement using a quadrupole mass spectrometer and a ultrahigh vacuum pressure gauge. The detailed method is described in the supplementary material and the previous papers. A summary of the characterization of the velocity-selected CH$_3$CN molecules is given in Fig. 2.

Additionally, the kinetic ion temperature of sympathetically cooled Ne$^+$ ions is needed to determine the translational reaction temperature for CH$_3$CN + Ne$^+$ $\rightarrow$ products. Although the energy distribution of sympathetically cooled ions is probably not thermal, the average ion kinetic energy ($T_{\text{ion}}$) of the trapped ions was used as a guide for evaluating the translational reaction temperature for the present experimental study. $T_{\text{ion}}$ was determined by comparing the observed laser-induced fluorescence (LIF) images of dual-species Coulomb crystals with the simulated images obtained by classical molecular dynamics (MD) simulations, which consider the time-dependent rf fields, laser cooling, and collision heating. The detailed method has been discussed in the previous paper and a summary is given in the supplementary material.

Describing the results, the average kinetic energy of Ne$^+$ ions slightly decreases with the decrease in the number of Ne$^+$ ions and does not strongly depend on the number of Ca$^+$ ions and the shape of the crystal. The average kinetic energy difference between the initial and final number of Ne$^+$ ions is expected to be lower than 1.0 K. According to the present experimental conditions, the average kinetic energy is confidently evaluated to be $T_{\text{ion}} = 1.8(0.5)$ K. The reaction translational temperature $T_{\text{tr}}$ is approximately determined by

$$T_{\text{tr}} = T_{\text{ion}} \frac{\mu}{M_{\text{ion}}} + T_{\text{PM}} \frac{\mu}{M_{\text{PM}}},$$

(1)
where \( \mu = M_{\text{ion}}M_{\text{PM}}/(M_{\text{ion}} + M_{\text{PM}}) \) is the reduced mass of the ion \((M_{\text{ion}})\) and the molecule \((M_{\text{PM}})\).\(^{32–35}\)

### B. Reaction rate measurement

In the present experiment, first, we start with preparing a \( \text{Ca}^+ \) Coulomb crystal by laser cooling trapped \( \text{Ca}^+ \), and then, we introduce neon gas of typically \( 5 \times 10^{-6} \) Pa into the ion trap chamber and produce \( \text{Ne}^+ \) ions by electron impact ionization. The electron beam energy is 250 eV and the electron current is about 0.5 nA at the ion trap. After a few minutes, a mixed ion Coulomb crystal consisting of \( \text{Ca}^+ \) and \( \text{Ne}^+ \) is produced. Since the trapping potential for \( \text{Ne}^+ \) ions is deeper than that of \( \text{Ca}^+ \), the \( \text{Ne}^+ \) ions distribute around the trap axis and a dark area appears in the LIF image of the \( \text{Ca}^+ \) Coulomb crystal.

The detailed procedure to determine the relative number of sympathetically cooled ions has been discussed previously\(^{34,35}\) and the summary is given in the supplementary material. In brief, the absolute number of sympathetically crystallized \( \text{Ne}^+ \) ions is proportional to the volume of the dark area in the LIF image of a dual-species Coulomb crystal because of an approximately constant number density of cold ions in an LPT. Therefore, the relative number of \( \text{Ne}^+ \) ions can be obtained by measuring the volume of the dark area in the LIF images under the assumption of the cylindrical symmetry of the spatial distribution of \( \text{Ne}^+ \) ions.\(^{35}\) Finally, the relative number of \( \text{Ne}^+ \) as a function of the reaction time with the velocity-selected \( \text{CH}_3\text{CN} \) molecules provides us the reaction rate of the \( \text{CH}_3\text{CN} + \text{Ne}^+ \rightarrow \) products with reliable accuracy based on the comparison of the gain of the kinetic energy of the reaction products with the depth of the trapping potential. The determination of the reaction branching ratio by time-of-flight mass spectrometry of ejected mixed ion Coulomb crystals\(^{33,51,52}\) is the next step of our project.

### III. THE PRS ION-DIPOLE CAPTURE RATE CONSTANT

We have calculated capture cross sections for ion collisions with \( \text{CH}_3\text{CN} \) molecules by the perturbed rotational state (PRS) theory.\(^{41–45}\) Here, we assume that the \( \text{CH}_3\text{CN} \) molecule is a symmetric-top rigid rotor and that the intermolecular interaction \( V \) between the \( \text{CH}_3\text{CN} \) molecule and an ion is given by the asymptotic forms of the dipole and the spherically symmetric polarization potentials. Introducing the rotational constants \( A_{\text{rot}}, B_{\text{rot}}, \) and \( C_{\text{rot}} = A_{\text{rot}} \), we can write the kinetic energy of the free rotation in the form

\[
\hat{H}_{\text{rot}} = B_{\text{rot}} \hbar^2 \hat{J}^2 + (A_{\text{rot}} - B_{\text{rot}}) \hbar^2 \hat{J}_0^2,
\]

where \( \hat{J} \) is the angular momentum vector of the molecule, \( \hat{J}_0 \) is its projection on the symmetry axis of the molecule, and the tilde denotes the quantum mechanical operator. The free rotational energy is given by

\[
E_{\text{JK}} = B_{\text{rot}} (J + 1) + (A_{\text{rot}} - B_{\text{rot}}) K^2,
\]

where \((J, K)\) are the rotational quantum numbers. In the PRS theory, the adiabatic picture is assumed for the rotational motion during the collision. We numerically diagonalize the Hamiltonian \( \hat{H}_{\text{PRS}} \) at each fixed intermolecular distance \( R \).\(^{41,42}\) Let \( \epsilon_{\text{JKM}}(R) \) be the diagonalized eigenvalue, which may be called an adiabatic potential. The adiabatic potential \( \epsilon_{\text{JKM}}(R) \) has the asymptotic form

\[
\epsilon_{\text{JKM}}(R) \sim E_{\text{JK}} \quad R \rightarrow \infty
\]

and can be identified by the quantum numbers \((J, K, M)\), with \( M \) being the magnetic quantum number along the intermolecular axis. We assume that the intermolecular motion is effectively governed by the adiabatic potential. As \( R \rightarrow \infty \), \( \epsilon_{\text{JKM}}(R) - E_{\text{JK}} \) becomes \( \propto R^{-2} \) for \( K \neq 0 \) and \( \propto R^{-4} \) for \( K = 0 \).\(^{31,45}\) Therefore, we can expect a drastic effect on the intermolecular motion in low-energy collisions of the symmetric-top molecule having \( K \neq 0 \).
By using the PRS adiabatic potential, we can obtain the orbiting impact parameter $b_{JKM}(E)$ as a function of collision energy $E$. The capture cross section (called the “hitting cross section” in Ref. 44) is defined by $\sigma(J, K, M) = \pi[b_{JKM}(E)]^2$. Since the orientation of the molecular axis of a velocity-selected CH$_3$CN is random to the position of the sympathetically cooled Ne$^+$ ions under the present experimental conditions, we need the $M$-average capture cross sections $\sigma(J, K) = (2J + 1)^{-1} \sum_M \sigma(J, K, M)$. Figure 3 shows example plots of the $M$-average cross sections as a function of collision energy. We calculated the ion–dipole capture cross sections up to $J = 60$ for the present system: About 30 000 of the cross sections curves were considered. Since the cross sections can be calculated only for a finite number of energies, the cross section values needed for the calculation of rate constants were obtained through spline interpolation.

The state-specific capture rate constants $k(J, K)$ are calculated by convolution of the collision energy dependence of the cross sections with the collision energy distribution between CH$_3$CN and Ne$^+$. The latter can be evaluated by $T_{tr}$ obtained from Eq. (1) by applying the Maxwell Boltzmann distribution $f_{tr}(E)$. We calculate the state-specific capture rate constant according to

$$k(J, K) = \int_{E_{min}}^{E_{max}} \sigma(J, K)f_{tr}(E)\sqrt{EdE}, \quad (4)$$

**FIG. 3.** Examples of $M$-average ion–dipole capture cross sections for the CH$_3$CN-ion system. The rotational level $(J, K)$ corresponding to each curve is indicated in the figure.

**FIG. 4.** Comparison between experiment (lower) and simulation (upper) for the longitudinal velocity distributions of the velocity-selected CH$_3$CN. Each number indicated in the upper graphs shows a translational temperature derived from the nonlinear fit of $P_{1d}$ [for (a)–(e)] or $P_{cold}(v, 2)$ [for (f)] of the equations in the supplementary material to the simulation results. The experimentally measured $T_{PM}$ shown in the lower figures are the values in Fig. 2(b).
where $E_{\text{max}}$ ($E_{\text{min}}$) is the maximum (minimum) energy for the interpolated data.

To obtain the average capture rate constant $k_{\text{PRS}}$ corresponding to the experimental condition from $k(J, K)$, we need the information about rotational state distribution $\rho(J, K)$ of the velocity-selected acetonitrile molecules. Since we could not directly measure $\rho(J, K)$ of the velocity-selected CH$_3$CN molecules, it was evaluated by Monte–Carlo trajectory simulations. The details of the simulation method were described in our previous papers.\textsuperscript{34,40}

First, we calculated the Stark shift energies of all rotational levels of CH$_3$CN up to $J = 60$ as a function of the applied electric field strength and record least-square fit coefficients of each Stark shift curve fitted by the fourth-order polynomial function. Then, we randomly set the initial position and velocity of a polar molecule using uniform random numbers according to the Maxwell–Boltzmann distribution at the assumed temperature. We performed the numerical integration of the equation of motion for each polar molecule using the fourth order Runge–Kutta algorithm. The force acting on a polar molecule is obtained by the gradient of the fitted Stark shift curve, which depends on a molecular position under quadrupole fields in the guide electrodes. Finally, we recorded the position, velocity, intensity, and the rotational level of the velocity-selected molecule at some certain distances from the beam guide exit. We considered the rotational state distribution of the source gas and the degeneracy arising from nuclear spin statistics as the weight to the intensity of the velocity-selected polar molecules. Repeating the same calculations for all rotational levels considered, we obtained the renormalized $\rho(J, K)$ and the velocity distribution.

Figure 4 shows the comparison between simulation and experiment for the longitudinal velocity distributions of the velocity-selected CH$_3$CN molecules. The corresponding simulation results of rotational level distributions are shown in the upper graphs of Fig. 5. It is observed that the rotational levels with the smaller Stark shift lead to a smaller population. In the lower graphs in Fig. 5, we also show the thermal rotational distributions, which are obtained by assuming that the rotational temperatures are the same as the translational ones. Since a good agreement was obtained between the simulation and experiment for the longitudinal velocity distribution, we assumed that the simulation result of $\rho(J, K)$ reproduces the actual rotational level distribution of the velocity-selected CH$_3$CN molecules. Using the simulation results of $\rho(J, K)$, we can calculate the velocity-selected PRS capture rate constant by the following equation:

![Figure 5](image-url)

**FIG. 5.** Simulation results of rotational level populations $\rho(J, K)$ of the velocity-selected and thermal CH$_3$CN molecules. The upper graphs show the simulation results of the velocity-selected molecules with the translational temperatures $T_{\text{tr}}$ of (a) 11(1) K and (b) 63(2) K. The lower graphs are the populations with the corresponding thermal conditions, i.e., the rotational temperature $T_{\text{rot}}$ is the same as the translational one.
$k_{\text{PRS}} = \sum_{J} \sum_{K} p(J, K) k(J, K). \quad (5)$

IV. RESULTS AND DISCUSSIONS

To measure the translational temperature dependence of the reaction rate constant of the CH$_3$CN + Ne$^+$ → product, we used two types of the Stark velocity filters as mentioned above. A cold CH$_3$CN molecular beam of a few kelvin was generated by the standard type Stark velocity. On the other hand, higher translational temperatures can be obtained using the wavy Stark velocity filter. We changed the guide voltages $|V_{\text{G}}|$ of the wavy Stark velocity filter from 0.4 kV to 2.0 kV, which resulted in the change in the translational temperature of the velocity-selected CH$_3$CN from 13(2) K to 60(1) K under the present experimental conditions.

In the reaction rate measurements, we first generated a two-component ion Coulomb crystal consisting of Ca$^+$ and Ne$^+$ ions and observed the decrease in the dark area occupied by Ne$^+$ ions with increasing reaction time with the velocity selected CH$_3$CN molecules. The experimental details are provided in the supplementary material.

Figure 6 shows plots of the relative number of Ne$^+$ ions as a function of the reaction time at some different translational temperatures of the velocity-selected CH$_3$CN molecules. As the number density of the velocity-selected molecules drastically increases with the increase in the guide voltages $|V_{\text{G}}|$ in the case of the wavy Stark velocity filter, the reaction rate becomes faster as $|V_{\text{G}}|$ increases in the measurements. It should be noted that our previous experiments suggested that a small number of residual ions, possibly NeH$^+$, were present. The fraction of the residuals in the dark area was less than 5% of the initial number of Ne$^+$ ions after a long reaction time of over 3000 s. Therefore, in the present reaction rate measurement, the systematic error due to the residual ions is evaluated to be 5%, and we included this error into the uncertainty of each measured reaction rate.

The pseudo-first-order reaction rate $y$ is transformed to the reaction rate constant $k$ by the relation of $k = y/n$, where $n$ is the number density of the velocity-selected CH$_3$CN at the ion trap position, as shown in Fig. 2. Figure 7 shows the translational temperature dependence of the reaction rate constant obtained by the present experiment. We also plot the velocity-selected PRS capture rate constant $k_{\text{PRS}}$ described in Sec. III.

A strong translational temperature dependence on the experimental reaction rate constant is observed particularly at the lower temperature than 5 K. In contrast, the velocity-selected PRS rate constants show a weak temperature dependence over the whole range of temperatures. The PRS result is consistent with the experimental value at a few kelvin but deviates significantly at the higher translational temperatures. It can be noted that the experimental rate constants are even smaller than the Langevin rate constant $k_l$ at temperatures higher than 10 K.

We regard the capture rate constant $k_{\text{cap}}$ as the upper limit of the reaction rate constant. Hence, we can set $k = P_{\text{react}}k_{\text{cap}}$, with $P_{\text{react}} \leq 1$ being the reaction probability. Figure 7 shows $P_{\text{react}} \approx 1$ at $T_{\text{tr}} \approx 2.7$ K and $P_{\text{react}} \ll 1$ at $T_{\text{tr}} > 5$ K. Unexpected small reaction rate constants (namely, $P_{\text{react}} \ll 1$) at room temperature have been reported in similar reactions such as Ne$^+$ + (H$_2$O and NH$_3$). In the present experiment, as the rotational state distribution $p(J, K)$ of the velocity-selected molecules is not strongly dependent on the applied guide voltages (see Fig. 5), the rapid variation in $k$ at $T_{\text{tr}} > 5$ K is not due to the difference in the rotational state distributions. Further experiments at different source gas temperatures may be interesting for understanding the reaction mechanism. We have a plan to perform such experiments using a cold buffer gas.

![FIG. 6. Reaction rate measurements between the velocity-selected CH$_3$CN molecules and cold Ne$^+$ ions. The relative number of sympathetically cooled Ne$^+$ ions are plotted as a function of the reaction time. The measurements (a)–(c) were performed by the wavy Stark velocity filter while (d) by the standard type. The applied guide voltages $|V_{\text{G}}|$ are (a) 0.4 kV, (b) 0.8 kV, (c) 2.0 kV, and (d) 3.0 kV, respectively.](image)

![FIG. 7. Comparison of the experimental rate constants with various capture rate constants: (a) the velocity-selected PRS capture rate constant, (b) present experimental work, (c) the thermal PRS capture rate constant (see the text), (d) Langevin rate constant, and (e) Su–Chesnavich expression of the ion–dipole capture rate constant obtained by classical trajectory calculations. The lines between plot points are guides for the eyes.](image)
cell for systematically changing $p(I, K)$. One possibility to explain $P_{\text{react}} \ll 1$ and its strong translational temperature dependence is the presence of a small potential barrier along the reaction path. In this type of reaction, a quantum chemistry calculation \cite{1} and \cite{2} shows that the rate constant has a minimum value at a certain temperature ($T_0$) associated with the potential barrier height: the increase in the rate constant with decreasing $T_0$ below $T_0$ occurs owing to the tunneling effect. Such temperature dependence was experimentally observed in $\text{NH}_3 + \text{H}_2 \rightarrow \text{NH}_4^+ + \text{H}_2$. \cite{3,4,5} Also in the present system, the reaction rate measurements above 20 K might demonstrate the increase with increasing $T_0$, and then, it would give us the information about the height of the potential barrier. It is very important to theoretically determine the potential energy surface relevant to intermediate and transitions states of the $\text{CH}_3\text{CN–Ne}^+$ system. In the future, we plan to carry out the quantum chemistry calculation.

V. FURTHER DISCUSSION

In Fig. 7, we plot the thermal PRS capture rate constants calculated by assuming the thermal distribution of the translational and rotational motion, as well as those obtained by the Su–Chenavich expression, which was obtained by performing classical trajectory Monte–Carlo calculations. \cite{6,7} and \cite{8} Su and Chenavich have found that the thermal ion–dipole capture rate constant $k_{\text{th}}(T)$ divided by the Langenov rate constant $k_L$ can be empirically given for various kinds of the ion–molecule system by

$$
\frac{k_{\text{th}}(T)}{k_L} = 0.4767x + 0.62, \quad x \geq 2, \quad \text{(6)}
$$

which is only a function of $x = D/(2\alpha k_B T)^{1/2}$, with $D$ being the dipole moment, $\alpha$ being the polarizability, and $T$ being the temperature. This is a very simple relation and has been occasionally used in estimating unknown values of reaction rate constants in astrochemical studies. \cite{9,10} Figure 7 shows that the thermal PRS capture rate constants are in good agreement with the values obtained by Eq. (6) for the present reaction system. Similar results were obtained for other polar molecules in a previous study. \cite{11}

However, Fig. 7 further shows that the thermal PRS capture rate constants are completely different from the velocity-selected $\text{CH}_3\text{CN}$ molecules, (ii) the evaluation of the reaction temperature, and (iii) the details of the reaction rate measurements.

VI. CONCLUSION

We have measured the translational temperature dependence of the reaction-rate constant of the $\text{CH}_3\text{CN} + \text{Ne}^+ \rightarrow \text{products}$ by applying two types of the Stark velocity filters, i.e., the standard type Stark velocity filter and the wavy Stark velocity filter. A steep increase in the reaction rate constant has been observed at temperatures lower than 5 K. To clarify the translational temperature dependence of the reaction probability, the PRS capture rate constants have been evaluated. The PRS theory reproduces well the experimental reaction rate constant at a few kelvin but not higher than 5 K. The difference between experiment and theory indicating the smaller reaction probability than unity may show the presence of a potential barrier in the reaction path. Further measurements at different source gas temperatures and at higher translational temperatures are expected to reveal the reaction mechanisms. Such measurements can be performed by using a cold buffer gas cell \cite{12} and the wavy Stark velocity filter with a larger curvature radius. \cite{13} The experiment using an upgraded buffer gas cell connected to the wavy Stark velocity filter will be performed in the future work.

The present research method combining the reaction rate measurements with the theoretical calculations of the PRS capture rate constants is very effective to elucidate both the translational and rotational temperature dependence of the reaction probability in cold ion–polar molecule reactions related to interstellar chemistry.

SUPPLEMENTARY MATERIAL

See the supplementary material for (i) the determination of the number density and translational temperatures of the velocity-selected $\text{CH}_3\text{CN}$ molecules, (ii) the evaluation of the reaction temperature, and (iii) the details of the reaction rate measurements.

ACKNOWLEDGMENTS

This work was supported, in part, by the JSPS KAKENHI Grant No. 18H01271, the Robert A. Welch Foundation under Grant No. A1546, and the Matsuo Foundation.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES
