



ABSOLUTE INTEGRAL CROSS SECTIONS FOR THE STATE-SELECTED ION–MOLECULE REACTION $\text{N}_2^+(\text{X}^2\Sigma_g^+; v^+ = 0-2) + \text{C}_2\text{H}_2$ IN THE COLLISION ENERGY RANGE OF 0.03–10.00 eV

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ABSTRACT

Using the vacuum ultraviolet laser pulsed field ionization-photoion source, together with the double-quadrupole–double-octopole mass spectrometer developed in our laboratory, we have investigated the state-selected ion–molecule reaction $\text{N}_2^+(\text{X}^2\Sigma_g^+; v^+ = 0-2, \text{N}^+ = 0-9) + \text{C}_2\text{H}_2$, achieving high internal-state selectivity and high kinetic energy resolution for reactant N_2^+ ions. The charge transfer (CT) and hydrogen-atom transfer (HT) channels, which lead to the respective formation of product C_2H_2^+ and N_2H^+ ions, are observed. The vibrationally selected absolute integral cross sections for the CT [$\sigma_{\text{CT}}(v^+)$] and HT [$\sigma_{\text{HT}}(v^+)$] channels obtained in the center-of-mass collision energy (E_{cm}) range of 0.03–10.00 eV reveal opposite E_{cm} dependences. The $\sigma_{\text{CT}}(v^+)$ is found to increase as E_{cm} is decreased, and is consistent with the long-range exothermic CT mechanism, whereas the E_{cm} enhancement observed for the $\sigma_{\text{HT}}(v^+)$ suggests effective coupling of kinetic energy to internal energy, enhancing the formation of N_2H^+ . The $\sigma_{\text{HT}}(v^+)$ curve exhibits a step at $E_{\text{cm}} = 0.70-1.00$ eV, suggesting the involvement of the excited $\text{C}_2\text{H}_2^+(\text{A}^2\Sigma_g^+)$ state in the HT reaction. Contrary to the strong E_{cm} dependences for $\sigma_{\text{CT}}(v^+)$ and $\sigma_{\text{HT}}(v^+)$, the effect of vibrational excitation of N_2^+ on both the CT and HT channels is marginal. The branching ratios and cross sections for the CT and HT channels determined in the present study are useful for modeling the atmospheric compositions of Saturn’s largest moon, Titan. These cross sections and branching ratios are also valuable for benchmarking theoretical calculations on chemical dynamics of the titled reaction.

Key words: astrochemistry – methods: laboratory: molecular – planets and satellites: atmospheres – planets and satellites: individual (Saturn, Titan)

1. INTRODUCTION

Gaseous ion–molecule reactions occur in many environments, such as interstellar clouds (Bohme 1992; Snow & Bierbaum 2008, p. 229), cometary comae (Giguere & Huebner 1978; Huntress et al. 1980), terrestrial atmospheres (Smith & Spanel 1995), plasma (Williams et al. 2002), and combustion (Semo & Koski 1984), with temperature ranging from a few tens of kelvin to as high as 10^6 K, and particle densities from 10^3 to 10^{20} cm $^{-3}$. In the past several decades, numerous experimental studies have been performed by employing a variety of experimental schemes (Ferguson 1975; Gerlich 1993; Dressler et al. 2006; Larsson et al. 2012; Geppert & Larsson 2013), aiming to gain fundamental understanding of ion–molecule collisions. Among previous studies, the state-selected ion–neutral collision approach, which involves reaction cross-section measurements as a function of kinetic and internal energies of the reactant ions, has been demonstrated to be among the most valuable schemes for the quantitative characterization of ion reactivity (Ng 2002b; Dressler et al. 2006).

The main difficulty involved for employing the state-selected ion–molecule collision approach is in the preparation of state-selected reactant ions. Ideally, reactant ions should not only be prepared with high quantum state purity and high kinetic energy resolution but also be produced with a sufficiently high intensity for experiments to be performed under single-collision conditions. Due to the fine control of photon energy and the more relaxed selection rules for photoionization transitions compared with those for direct ion photoexcitation, the single-photon vacuum ultraviolet (VUV) photoionization technique is most suitable for the preparation of state-selected reactant ions (Chupka & Russell 1968). For example, metastable ion

states, which cannot be produced by direct ion photoexcitation, can be prepared readily by VUV photoionization (Ng 1991, 2002a, 2014). For the use of a continuum discharge or a synchrotron-based pseudocontinuum VUV photoionization source, state-selected ions have been successfully prepared by using the photoelectron–photoion coincidence method for state-selected ion–molecule reaction studies. With the use of a pulsed VUV laser photoionization source, such as that in the present experiment, state-selected ions can be generated by using the VUV mass analyzed threshold ion method, which is referred to here as the VUV pulsed field ionization-photoion (VUV-PFI-PI) technique. By combining the VUV-PFI-PI and the photoelectron–photoion secondary coincidence detection schemes in a synchrotron-based study, we have successfully examined the absolute integral cross sections for the formation of RgH^+ ions from the state-selected collisions of $\text{H}_2^+(v^+ = 0-17, \text{N}^+)$ [$\text{HD}^+(v^+ = 0-17, \text{N}^+)$] + Rg, where Rg = He, Ne, and Ar (Dressler et al. 2006). Using a VUV laser PFI-PI source, we have also measured previously the absolute integral cross sections for the rovibrationally selected $\text{NO}^+(v^+ = 0-2, \text{N}^+) + \text{Ar}$ charge transfer (CT) reaction, achieving high internal-state selectivity (Dressler et al. 2006). However, the achieved kinetic energy spread for reactant NO^+ ions is larger than 1 eV, preventing the cross-section measurement from being made down to the thermal energy range, which is recognized to be important for astrochemical studies.

Recently, we have made significant progress in achieving high kinetic energy resolution for the preparation of state-selected reactant PFI-PIs. By applying a novel electric field pulsing sequence to the VUV laser PFI-PI reactant ion source, we show that the laboratory kinetic energy (E_{lab}) spread of reactant PFI-PIs can be narrowed down to $\Delta E_{\text{lab}} = \pm 50$ meV, thus allowing the experimental cross-

section measurement for state-selected ion–molecule reactions to be performed down to thermal energies (30–50 meV; Chang et al. 2011, 2012). Using this VUV-PFI-PI source to prepare state-selected reactant ions along with the double-quadrupole–double-octopole (DQDO) ion guide mass spectrometer developed in our laboratory, we have obtained detailed absolute integral cross sections for the ion–molecule reaction systems, $\text{N}_2^+(X^2\Sigma_g^+; v^+ = 0-2; N^+ = 0-9) + \text{Ar} (\text{CH}_4)$ (Chang et al. 2011, 2012; Xu et al. 2013a; Ng 2014) and $\text{H}_2\text{O}^+(X^2B_1; v_1v_2v_3 = 000, 100, \text{ and } 020; N^+_{\text{Ka+Kc+}} = 0_{00-322}) + \text{H}_2 (\text{D}_2)$ (Xu et al. 2012, 2013b; Li et al. 2014), covering the center-of-mass collision energies (E_{cm}) from 30 meV to 10.00 eV, as well as a wide range of rotational and vibrational states of the reactant ions. In the present work, we have extended the investigation on the effect of vibrational excitation and collision energy to the absolute integral cross sections and branching ratios of the vibrationally state-selected ion–molecule reaction system $\text{N}_2^+(X^2\Sigma_g^+; v^+ = 0-2) + \text{C}_2\text{H}_2$.

Titan, the largest moon of Saturn, has garnered intense research interest in recent years (Anicich & McEwan 1997; Bird et al. 1997; Lindal et al. 1983; Nagy & Cravens 1998; Niemann et al. 2005; Shemansky et al. 2005; Vuitton et al. 2006; Schinder et al. 2011), partially due to its substantial atmosphere, harboring one of the richest atmospheric chemistries in the solar system, which culminates in the generation of thick haze layers. Based on the measurements (Lindal et al. 1983; Bird et al. 1997; Schinder et al. 2011) by the *Voyager* spacecraft in the 1980s and by the *Cassini/Huygens* mission since 1997, in which the *Huygens* probe was successfully landed on Titan’s surface (Lebreton et al. 2005; Niemann et al. 2005) in 2005, N_2 was determined as the dominant species, along with the detection of CH_4 , C_2H_2 , and C_2H_4 molecules as the most abundant hydrocarbons in the atmosphere of Titan. Thus, the interactions of these chemical species are believed to be responsible for the complex nitrogen-enriched organic chemistry reaction cycles occurring in Titan’s atmosphere. Neutral N_2 molecules in the upper atmosphere can be ionized by the solar radiation, energetic particles, and cosmic rays, to produce N_2^+ ions in different v^+ vibrational states. The fact that 94% of the Titan atmosphere is N_2 results in N_2^+ being one of the major ion species in Titan’s atmosphere. The ion–molecule reactions between N_2^+ and the hydrocarbon species, CH_4 , C_2H_2 , and C_2H_4 , are considered to be one of the most important processes that trigger the overall ion chemistry of Titan’s atmosphere (Anicich & McEwan 1997; Vuitton et al. 2007). Since vibrationally excited $\text{N}_2^+(X^2\Sigma_g^+; v^+ \geq 1)$ ions have long lifetimes, the ion–molecule reactions between vibrationally excited $\text{N}_2^+(X^2\Sigma_g^+; v^+ \geq 1)$ ions and simple hydrocarbons are expected to play a role in the atmospheric chemistry of Titan.

Compared with the ion–molecule reaction system of $\text{N}_2^+ + \text{CH}_4$ (see, e.g., Xu et al. 2013a, and references therein), only a few experimental studies have been reported on the $\text{N}_2^+ + \text{C}_2\text{H}_2$ ion–molecule reaction system. In 1971, Dreyer & Perner (1971) investigated the latter ion–molecule reaction by using the kinetic absorption spectroscopy method. Only the CT channel was measured, and the rate constant at room temperature was determined as $(8.8 \pm 1.0) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, which was compared with the prediction of $1.30 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ by the Langevin–Gioumousis–Stevenson (LGS) orbiting model (Gioumousis & Stevenson 1958). A

$(4.00 \pm 1.00) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ was reported by Anicich & McEwan (1997) using the ion cyclotron mass spectrometric technique. In addition to the CT channel of forming C_2H_2^+ ions, two other reaction channels leading to the formation of HCN^+ and N_2H^+ ions were also reported. The branching ratios for the above three product channels associated with the formation of C_2H_2^+ , HCN^+ , and N_2H^+ ions were determined to be 0.37:0.03:0.60. Recently, Gichuhi & Suits (2011) have reinvestigated the $\text{N}_2^+ + \text{C}_2\text{H}_2$ reaction at a temperature of $40 \pm 5 \text{ K}$ by employing a velocity-map-imaging mass spectrometer, in which the C_2H_2^+ ion was observed as the sole product ion. To resolve the discrepancies of product ions and branching ratios observed in previous studies requires a detailed experimental study with well-defined internal reactant states and collision energies. To our best knowledge, a detailed quantum state or temperature dependence study on this reaction system has not been reported.

2. EXPERIMENTAL CONSIDERATIONS

Since the experimental arrangement and procedures for using the VUV laser PFI-PI reactant ion source and the DQDO ion guide apparatus in the present work are similar to those described in detail in previous studies (Chang et al. 2011, 2012; Xu et al. 2013a), only a brief description is given below.

VUV laser radiation. In order to prepare reactant N_2^+ ions in the ground electronic state with the internal vibrational excitation of $v^+ = 0, 1, \text{ or } 2$ by using the single-photon VUV-PFI-PI technique, the VUV laser radiation generated by the resonance-enhanced four-wave frequency mixing scheme in Kr gas as the nonlinear medium is adopted. Here the VUV laser in the range of $125,500\text{--}130,200 \text{ cm}^{-1}$ generated by the sum frequency ($2\omega_1 + \omega_2$) mixing is used, where ω_1 and ω_2 represent the outputs of the ultraviolet (UV) and visible (VIS) dye lasers, respectively. The second and third harmonic output of an identical Nd-YAG laser (Spectra-Physics, Model PRO-290) operated in 15 Hz is employed to pump the UV and VIS dye lasers, respectively. A dichroic mirror is used to merge the UV ω_1 and the VIS ω_2 dye laser outputs at a Kr gas jet. Here the UV ω_1 output is fixed at 212.556 nm so that the two-photon frequency $2\omega_1$ matches the $4p \rightarrow 5p$ resonance transition of the Kr atom, and the VIS ω_2 output is tuned in the range of 270–325 nm to generate the VUV sum frequencies required for the experiment.

Since no diffraction grating or separation lens is employed in the present experiment, the sum frequency ($2\omega_1 + \omega_2$), the different frequency ($2\omega_1 - \omega_2$), the tripling frequency ($3\omega_1$), and the fundamental frequencies (ω_1 and ω_2) all enter the photoionization/photoexcitation (PI/PEX) region and intersect the N_2 supersonic molecular beam at 90° . Due to the high ionization energy (IE) of N_2 , only the sum frequency and the tripling frequency can photoionize N_2 . On the basis of spectral simulation of the measured VUV-PFI-PI spectrum for $\text{N}_2^+(X; v^+ = 0-2, N^+)$, we conclude that the tripling frequency of $3\omega_1$ makes no contribution to the observed N_2^+ PFI-PIs, and the PFI-PIs are solely generated by the VUV laser sum frequency output.

VUV laser PFI-PI reactant ion source. The rovibrationally selected $\text{N}_2^+(X^2\Sigma_g^+; v^+ = 0-2, N^+ = 0-9)$ reactant ions are produced here by PFI of excited N_2 molecules in high- n ($n \geq 100$) Rydberg states [$\text{N}_2^*(n)$] converging to the ionization thresholds of interest by VUV laser photoexcitation of cold N_2 molecules at the PI/PEX center. The $\text{N}_2^*(n \geq 100)$ Rydberg

species formed by VUV photoexcitation of N_2 can be considered to consist of an ion core with well-defined rovibronic quantum numbers and a weakly bound Rydberg electron at an energy of $2\text{--}4\text{ cm}^{-1}$ below the ion core converging limit. Thus, the formation of the ion core state of interest can be accomplished by Stark field ionization of the Rydberg species using a small PFI field (Chang et al. 2011, 2012; Xu et al. 2013a). In the present study, for each PFI-PI vibrational band, N_2^+ ions were prepared by setting the VUV laser frequency at the strongest rotational peak position, i.e., the Q branch. The vibrationally selected $N_2^+(v^+ = 0\text{--}2)$ ions thus prepared are in a distribution of low rotational $N^+ = 0\text{--}9$ states (Chang et al. 2012). The most important requirement to generate state-selected $N_2^+(X^2\Sigma_g^+; v^+ = 0\text{--}2, N^+)$ PFI-PIs is to spatially separate background prompt ions formed by direct photoionization of N_2 and reject these prompt ions from entering the radio frequency (rf) octopole ion guide reaction gas cell, where the reaction between N_2^+ and C_2H_2 occurs.

The PFI-PI reactant ion source used essentially consists of three circular aperture ion lenses 1, 2, and 3. The PI/PEX region is defined by the region between ion lenses 1 and 2. Cold N_2 molecules in the form of a supersonic molecular beam travel along the central axis of ion lenses 1–3 and enter the PI/PEX region through ion lens 1 to intersect the VUV laser beam. After a delay of 150 ns measured with respect to the VUV laser photoexcitation pulse, a pulsed electric field (magnitude = 2 V cm^{-1} , duration = $2\text{ }\mu\text{s}$) is applied to ion lens 2 to retard the background prompt ions, while the excited $N_2^*(n)$ molecules with long lifetimes continue to travel along the N_2 molecular beam direction, resulting in the separation of the prompt ions from excited $N_2^*(n)$ molecules. Immediately following the ending of the retarding electric field pulse, a pulsed electric field (magnitude = 15 eV cm^{-1} , duration = $0.5\text{ }\mu\text{s}$) is applied to ion lens 1. This PFI pulse serves to Stark field ionize the $N_2^*(n)$ molecules and extract the resulting N_2^+ PFI-PIs toward the rf-octopole reaction gas cell. In order to assure that all the N_2^+ PFI-PIs gain the same kinetic energy, the key is turning on the PFI pulse only for $0.5\text{ }\mu\text{s}$ such that the PFI-PIs are in the uniform electric field of the PI/PEX region during the PFI and the PFI-PI acceleration. Since the PFI field is turned off before PFI-PIs exit the PI/PEX region through ion lens 2, the PFI-PIs are expected to gain the same kinetic energy and have the minimal laboratory kinetic energy spread ($\Delta E_{\text{lab}} \approx \pm 50\text{ meV}$; Chang et al. 2012). The prompt ions are lagged by the retarding pulsed electric field and thus have smaller kinetic energies than the PFI-PIs. As a result, a small energy barrier applied to ion lens 3 can reject all prompt ions and pass only the N_2^+ PFI-PIs to enter the rf-octopole ion guide reaction gas cell for the ion–molecule collision of $N_2^+(X^2\Sigma_g^+; v^+ = 0\text{--}2) + C_2H_2$.

DQDO mass spectrometer. The DQDO mass spectrometer developed consists of, in sequential order, the VUV-PFI-PI reactant ion source as described above, a reactant quadrupole mass spectrometer (QMS), an rf-octopole ion guide reaction gas cell, and a product QMS. The reactant QMS can be used to select the reactant ions of interest. However, in the present experiment, the reactant QMS is only used as an ion lens for allowing all ions from the ion source to enter the rf-octopole ion guide reaction gas cell. The fact that N_2^+ ions are the only ionic species produced by VUV photoionization makes the mass selection by the reactant QMS unnecessary. The reaction

gas cell is situated between two rf-octopole ion guides, which are powered by the same rf power supply. The DC voltages applied to the two rf octopoles can be slightly different. This allows slow product ions to be effectively extracted from the reaction gas cell. The reaction gas cell is filled with the neutral C_2H_2 reactant gas at the pressure of 1.0×10^{-4} Torr, which is monitored by an MKS Baratron. All product ions produced in the reaction gas cell, along with the attenuated N_2^+ reactant PFI-PIs, are guided into the product QMS for the mass analysis. By selecting the mass-to-charge (m/z) ratios of product ions observed using the product QMS, the intensities of individual product ions can be measured. The product ions formed are counted by a multichannel scalar. The typical accumulation time for the measurement of N_2^+ PFI-PI ions is 60 s, and those for the product ions are 120 s. For ions with $m/z = 26\text{--}28$, the absolute detection efficiency is about 0.5–0.8.

The absolute integral cross-section curves for the product ions $C_2H_2^+$ and N_2H^+ obtained at $E_{\text{cm}} = 0.03\text{--}10.00\text{ eV}$ in the present study are the average of at least six independent measurements. In the present study, Equation (1) is used for the conversion of the E_{lab} to the E_{cm} :

$$E_{\text{cm}} = E_{\text{lab}} [M/(m^+ + M)]. \quad (1)$$

Here m^+ and M represent the mass of the N_2^+ ion and the C_2H_2 molecule, respectively. The run-to-run uncertainty is in the range of 10%–15%. However, the absolute integral cross section reported here depends on the calibrations of the reactant gas cell length and pressure used and is estimated to be 30% (Chang et al. 2011).

3. RESULTS AND DISCUSSIONS

Mass spectra. As an example, we show in Figure 1(a) a typical mass spectrum of the $N_2^+(X^2\Sigma_g^+; v^+ = 0, N^+)$ reactant ion source observed without filling the reactant C_2H_2 gas in the rf ion guide reaction gas cell. This mass spectrum reveals a strong ion peak at $m/z = 28$ and a very minor ion peak at $m/z = 29$, which are assigned as the $^{14}\text{N}^{14}\text{N}^+$ ion and the isotopic $^{15}\text{N}^{14}\text{N}^+$ ion, respectively. This assignment is based on the fact that the relative intensities of the $m/z = 28$ and $m/z = 29$ ion peaks agree with the natural isotope abundances of ^{14}N and ^{15}N . The mass spectrum shown in Figure 1(b) is recorded by keeping all experimental conditions identical to those used in measuring the spectrum of Figure 1(a), except that the rf-octopole reaction gas cell is filled by C_2H_2 to a gas pressure of 1.0×10^{-4} Torr. Thus, the mass spectrum of Figure 1(b) is a measure of the reactant and product ion intensities for the $N_2^+ + C_2H_2$ reaction system at $E_{\text{cm}} = 0.10\text{ eV}$. In Figure 1(b), three ion peaks are observed at $m/z = 26, 28$, and 29 , which are assigned as $C_2H_2^+$, N_2^+ , and $^{14}\text{N}^{15}\text{N}^+/N_2H^+$ ions, respectively. Since the N_2H^+ ion peak overlaps with the isotopic $^{14}\text{N}^{15}\text{N}^+$ ion peak in the mass spectrum of Figure 1(b), the intensity of the N_2H^+ ion is determined here by taking the difference of the $m/z = 29$ ion intensities observed with and without the reactant C_2H_2 filled in the reaction gas cell.

On the basis of the analyses and assignment of the reactant and product mass spectra observed at $E_{\text{cm}} = 0.10\text{ eV}$ as depicted in Figures 1(a) and (b), along with those observed at other E_{cm} values, we conclude that $C_2H_2^+$ and N_2H^+ ions are the primary product ions of the $N_2^+ + C_2H_2$ reaction at $E_{\text{cm}} = 0.03\text{--}10.00\text{ eV}$. These product ions are likely formed by the CT and hydrogen-atom transfer (HT) reactions shown in reactions (2.1) and (2.2), respectively. These reactions are

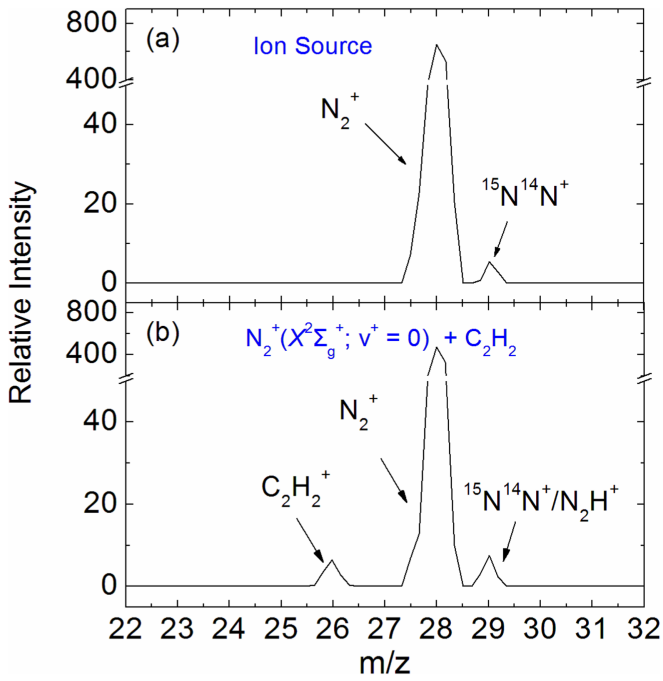
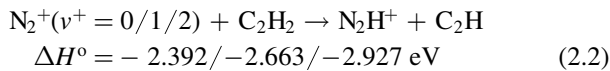
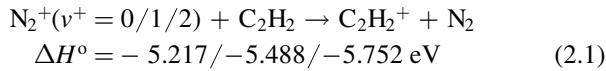


Figure 1. (a) Mass spectrum of the reactant N_2^+ PFI-PI source observed without filling the neutral reactant C_2H_2 gas in the rf-octopole ion guide reaction gas cell. Besides the $^{14}N^{14}N^+$ ion observed at $m/z = 28$, a very minor ion peak is also observed at $m/z = 29$, which is assigned as the isotopic $^{15}N^{14}N^+$ ion. (b) Mass spectrum recorded by keeping all experimental conditions identical to (a), except that the rf-octopole ion guide reaction gas cell is filled with C_2H_2 to the pressure of 10^{-4} Torr. The mass spectrum of (b) reveals three ion peaks at $m/z = 26, 28$, and 29 , which are assigned as $C_2H_2^+$, $^{14}N^{14}N^+$, and $^{15}N^{14}N^+/N_2H^+$. The product $C_2H_2^+$ and N_2H^+ ions are formed at $E_{cm} = 0.10$ eV.

highly exothermic (Lias et al. 1988), with the exothermicities of 5.22–5.75 eV for reaction (2.1) and 2.39–2.93 eV for reaction (2.2).



Due to the low intensity of N_2H^+ ions, this HT product channel was not observed in many previous experiments (Dreyer & Perner 1971; Gichuhi & Suits 2011). The HCN^+ product channel reported by Anicich & McEwan (1997) is also not observed in the present study. It was reported recently that for some reaction systems, the double HT channel can dominate over the single HT channel (O'Connor et al. 2015). For the present reaction system, we have looked into the possible formation of H_2CN^+ ions. Although the H_2CN^+ and N_2^+ ions have the same mass, the kinetic energy distribution of H_2CN^+ ions (if produced) is expected to be significantly different and broader compared to that of reactant N_2^+ ions because H_2CN^+ ions produced by the $N_2^+ + C_2H_2$ reaction should have different internal excitations, whereas reactant N_2^+ ions are formed in a supersonic beam and are rovibrationally cooled. Therefore, time-of-flight (TOF) measurements can differentiate the formation of N_2^+ from H_2CN^+ . We have previously used the TOF method to confirm the formation of $C_2H_4^+$ product ions, which has the same mass of the reactant N_2^+ ion in the ion-molecule reaction of $N_2^+ + CH_4$ (Xu

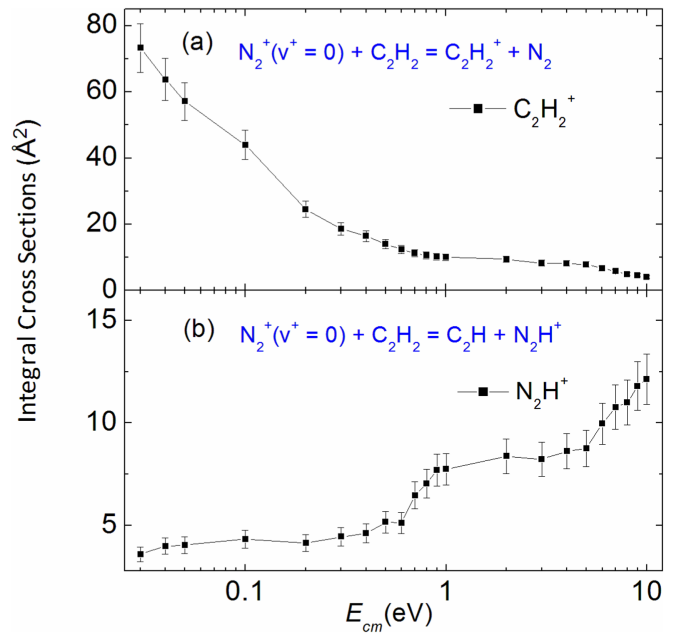


Figure 2. Comparison of the absolute integral cross section for the charge transfer [$\sigma_{CT}(v^+ = 0)$] and the H-atom transfer [$\sigma_{HT}(v^+ = 0)$] channel observed in the E_{cm} range of 0.03–10.00 eV.

et al. 2013a). On the basis of TOF measurements observed in the present study, we conclude that the H_2CN^+ ion is not produced in the ion-molecule reaction of $N_2^+ + C_2H_2$. The reactant and product mass spectra measured at different C_2H_2 pressures from 1×10^{-5} to 4×10^{-4} Torr used in the rf-reaction gas cell indicate that no ions are formed from secondary reactions in the present study.

Kinetic energy dependence. As described above, by changing the static voltage applied to the rf-octopole ion guide reaction gas cell, the kinetic energy of the reactant N_2^+ ion can be varied, and thus the $N_2^+ + C_2H_2$ reaction can be examined as a function of collision energy in the range of $E_{cm} = 0.03$ –10.00 eV. We arbitrarily set the highest $E_{cm} = 10$ eV because the strongest chemical bond is known to be 10 eV (for CO). The $E_{cm} = 0.03$ –10.00 range is the most interesting range for chemists. As demonstrated in previous experiments, the E_{cm} can readily be extended to higher energies (Ng 2002b). By using the product QMS to measure the intensities for the reactant N_2^+ ion and the corresponding product ions, the absolute integral cross section can be calculated by using the following formula:

$$\sigma = \frac{kT}{Pl} \ln \frac{I+i}{I}, \quad (3)$$

where σ represents the absolute integral cross section, k is the Boltzmann constant, T and P stand for the temperature and pressure of the neutral reactant gas, respectively, l is the effective length of the reaction gas cell, which has been calibrated in previous studies, I is the intensity of unreacted reactant N_2^+ ions, and i accounts for the sum of the intensities of product $C_2H_2^+$ and N_2H^+ ions.

The absolute integral cross sections (σ_{CT} and σ_{HT}) thus obtained for the CT and HT reaction channels of the titled reaction at $E_{cm} = 0.03$ –10.00 eV are depicted in Figures 2(a) and (b), respectively. As shown in these figures, the E_{cm} dependence of $\sigma_{CT}(v^+ = 0)$ is opposite compared to that of

$\sigma_{\text{HT}}(v^+ = 0)$. The $\sigma_{\text{CT}}(v^+ = 0)$ decreases from $73.1 \pm 7.0 \text{ \AA}^2$ at $E_{\text{cm}} = 0.03 \text{ eV}$ to $4.0 \pm 0.4 \text{ \AA}^2$ at $E_{\text{cm}} = 10.00 \text{ eV}$. In contrast, the $\sigma_{\text{HT}}(v^+ = 0)$ is found to increase from $3.6 \pm 0.4 \text{ \AA}^2$ to $12.1 \pm 0.4 \text{ \AA}^2$ as E_{cm} is changed from 0.03 to 10.00 eV. The opposite trends of E_{cm} dependences observed for $\sigma_{\text{CT}}(v^+ = 0)$ and $\sigma_{\text{HT}}(v^+ = 0)$ indicate that different reaction mechanisms are operative for the CT and the HT channels. The HT channels may be associated with a more direct short-range reaction mechanism, which becomes more efficient at higher collision energies. However, the CT reaction channels may be attributed to the long-range charge-induced dipole interaction mechanism. The detailed interpretation of the reaction mechanisms of reactions (2.1) and (2.2) would require a rigorous theoretical chemical dynamics study, which is beyond the scope of the present study. In two previous experiments (Orlando et al. 1990; Yang et al. 1991), the integral cross sections for product C_2HS^+ ions formed in the exothermic reactions of $\text{C}_2\text{H}_2^+ + \text{OCS}$ and $\text{OCS}^+ + \text{C}_2\text{H}_2$ show increasing trends as the E_{cm} is increased, similar to the trend of the N_2H^+ channel observed in the present experiment. We note that while the cross section for N_2H^+ is found to increase as the E_{cm} is increased, the sum of the cross sections for the formation of N_2H^+ and C_2H_2^+ from reactions (2.1) and (2.2) has a decreasing trend (see Figure 4).

The HT channel, i.e., the formation of N_2H^+ , was also observed in our previous study of the ion–molecule reaction $\text{N}_2^+ + \text{CH}_4$ (Xu et al. 2013a). The E_{cm} dependence of the $\sigma_{\text{HT}}(v^+ = 0)$ curve observed in the E_{cm} region of 0.03–10.00 eV for the later reaction is also found to have an opposite trend compared to that for the $\text{N}_2^+ + \text{C}_2\text{H}_2$ reaction. Here, for the $\text{N}_2^+ + \text{C}_2\text{H}_2$ reaction, a distinct step-like increase of $\sigma_{\text{HT}}(v^+ = 0)$ is observed in the E_{cm} range of 0.70–1.00 eV, which can be taken as evidence for the involvement of the excited $\text{C}_2\text{H}_2^+(A^2\Sigma_g^+)$ state along the HT pathway. In the previous He I photoelectron study (Reutt et al. 1986), the IE values for the formation of the $\text{C}_2\text{H}_2^+(X^2\Pi_u)$ and $A^2\Sigma_g^+$ states were determined as 11.403 and 16.297 eV, respectively. Taking into account that the $\text{IE}(\text{N}_2) = 15.581 \text{ eV}$, the first excited electronic state $\text{C}_2\text{H}_2^+(A^2\Sigma_g^+)$ is expected to become accessible when E_{cm} is greater than 0.72 eV. Compared with the distinct increase of $\sigma_{\text{HT}}(v^+ = 0)$ at $E_{\text{cm}} = 0.70\text{--}1.00 \text{ eV}$, the $\sigma_{\text{CT}}(v^+ = 0)$ only exhibits a slight decline at the same E_{cm} range, indicating that the accessibility to the excited $\text{C}_2\text{H}_2^+(A^2\Sigma_g^+)$ state only enhances the HT channel. While the $\sigma_{\text{CT}}(v^+ = 0)$ curve of Figure 2(a) is consistent with a long-range CT mechanism, the $\sigma_{\text{HT}}(v^+ = 0)$ may involve an efficient coupling between kinetic energy and internal vibrational energy, enhancing the formation of N_2H^+ in shorter ranges.

We note that the thermal motion of neutral reactant molecules C_2H_2 at room temperature $T = 298 \text{ K}$ can affect the kinetic energy resolution (ΔE_{cm}) for a given E_{cm} value. Chantry has shown that the ΔE_{cm} value or the Doppler width caused by the thermal motion of the target gas alone is equal to $(11.1\gamma kTE_{\text{cm}})^{1/2}$, where $\gamma = m^+/(m^+ + M)$ (Chantry 1971). The estimated thermal broadening for the present reaction system is about one order of magnitude smaller than the E_{cm} when $E_{\text{cm}} \geq 1.00 \text{ eV}$. But the thermal broadening becomes comparable with E_{cm} when $0.10 \text{ eV} \leq E_{\text{cm}} < 1.00 \text{ eV}$, and even larger than the E_{cm} when $E_{\text{cm}} < 0.10 \text{ eV}$. Because of the relatively large Doppler width at $E_{\text{cm}} < 0.10 \text{ eV}$, the measured $\sigma_{\text{CT}}(v^+ = 0)$ values at low E_{cm} values shown in Figure 2(a) could be distorted.

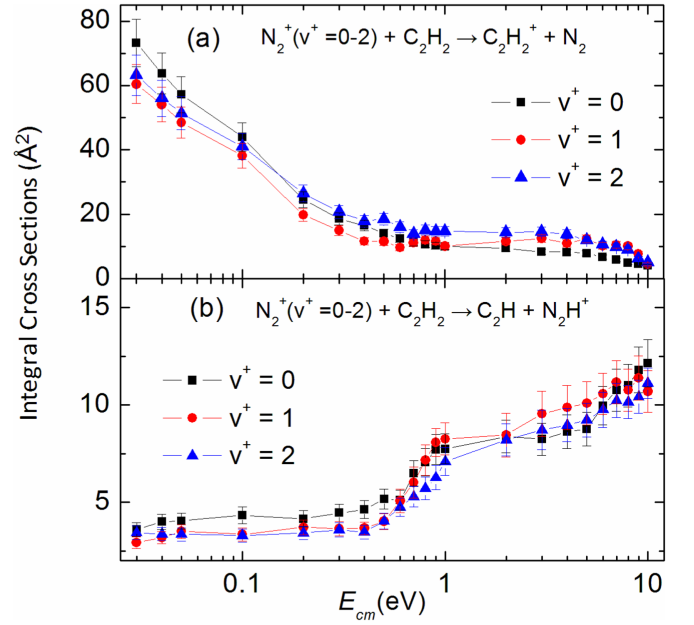


Figure 3. (a) Comparison of the absolute integral cross section for the charge transfer channels $\sigma_{\text{CT}}(v^+)$, for $v^+ = 0, 1$, and 2 , observed in the E_{cm} range of 0.03–10.00 eV. (b) Comparison of the absolute integral cross section $\sigma_{\text{HT}}(v^+)$, for $v^+ = 0, 1$, and 2 , observed in the E_{cm} range of 0.03–10.00 eV.

Vibrational-state dependence. In order to investigate the effect of vibrational excitation on the chemical reactivity of $\text{N}_2^+(X^2\Sigma_g^+; v^+)$ toward C_2H_2 , we have compared in Figures 3(a) and (b) the respective $\sigma_{\text{CT}}(v^+)$ and $\sigma_{\text{HT}}(v^+)$ curves obtained at $E_{\text{cm}} = 0.03\text{--}10.00 \text{ eV}$ with the reactant N_2^+ PFI-PIs prepared in the $v^+ = 0, 1$, and 2 vibrational states. As shown in the figures, after taking into account the experimental uncertainties, the $\sigma_{\text{CT}}(v^+)$ and $\sigma_{\text{HT}}(v^+)$ curves for $v^+ = 1$ and 2 vibrational states are found to be nearly in agreement with the corresponding $\sigma_{\text{CT}}(v^+ = 0)$ and $\sigma_{\text{HT}}(v^+ = 0)$ curves. Thus, we conclude that both the CT (reaction (2.1)) and the HT (reaction (2.2)) channels have only marginal vibrational effects. Nevertheless, the measured CT and HT cross sections seem to show weak vibrational inhibition at low E_{cm} values and weak vibrational enhancement at high E_{cm} values. In the range of $E_{\text{cm}} = 0.03\text{--}0.60 \text{ eV}$, the $\text{N}_2^+(v^+ = 1)$ state shows the lowest CT reactivity. For $E_{\text{cm}} > 0.60 \text{ eV}$, the CT cross section is higher for reactant N_2^+ ion in the $v^+ = 1$ and 2 states compared to that in the $v^+ = 0$ state. For the convenience of utilizing the results obtained here for atmospheric modelings, we have listed in Table 1 all integral cross sections plotted in Figures 2, 3(a), and 3(b).

In all previous studies of the $\text{N}_2^+ + \text{C}_2\text{H}_2$ reaction system (Dreyer & Perner 1971; Vuitton et al. 2007; Chang et al. 2011), the internal vibrational state of reactant N_2^+ ions was not selected, and in most previous experiments only the CT channel was reported. Thus, it is difficult to compare directly the results of previous studies with those obtained in the present study. Based on this consideration, we have taken the sum of $\sigma_{\text{CT}}(v^+) + \sigma_{\text{HT}}(v^+)$ to be a measure of the overall chemical reactivity of $\text{N}_2^+(v^+)$ toward C_2H_2 . The overall absolute integral cross sections, i.e., $\sigma_{\text{CT}}(v^+) + \sigma_{\text{HT}}(v^+)$, for $v^+ = 0, 1$, and 2 vibrational states, obtained in this experiment are depicted in Figure 4 for comparison with the results obtained by Dreyer & Perner (1971) (open black square) and by Anicich & McEwan (1997) (open black circle). The reaction

Table 1

Absolute Integral Cross Sections $\sigma(\text{\AA}^2)$ of the CT and HT Channels of the Vibrationally State-selected Ion–Molecule Reaction $\text{N}_2^+(X^2\Sigma_g^+; v^+ = 0-2) + \text{C}_2\text{H}_2$ Measured in the E_{cm} Range of 0.03–10.00 eV

$E_{\text{cm}}(\text{eV})$	$v^+ = 0$		$v^+ = 1$		$v^+ = 2$	
	σ_{CT}	σ_{HT}	σ_{CT}	σ_{HT}	σ_{CT}	σ_{HT}
0.03	73.3	3.6	60.4	2.9	63.2	3.4
0.04	63.7	4.0	54.1	3.2	56.0	3.4
0.05	57.1	4.0	48.5	3.5	51.4	3.4
0.10	44.0	4.3	38.2	3.4	41.0	3.3
0.20	24.6	4.2	19.7	3.7	26.5	3.4
0.30	18.6	4.5	15.0	3.6	20.7	3.6
0.40	16.5	4.6	11.6	3.7	17.9	3.5
0.50	14.0	5.2	11.5	4.0	18.5	4.0
0.60	12.4	5.1	9.7	5.1	16.0	4.8
0.70	11.2	6.5	11.1	6.0	13.9	5.3
0.80	10.6	7.1	12.0	7.2	15.1	5.7
0.90	10.2	7.7	11.6	8.1	14.7	6.3
1.00	10.0	7.7	10.1	8.3	14.7	7.1
2.00	9.4	8.4	11.5	8.5	14.4	8.2
3.00	8.3	8.2	12.5	9.5	14.5	8.7
4.00	8.2	8.6	11.0	9.9	13.7	9.0
5.00	7.9	8.8	12.3	10.1	11.9	9.2
6.00	6.7	10.0	10.2	10.6	10.6	9.8
7.00	5.8	10.8	10.5	11.2	9.8	10.2
8.00	4.9	11.0	10.0	10.8	9.0	10.2
9.00	4.6	11.8	7.7	11.4	6.2	10.4
10.00	4.0	12.1	4.4	10.7	5.0	11.1

Note. The run-to-run uncertainties are in the range of 10%–15%.

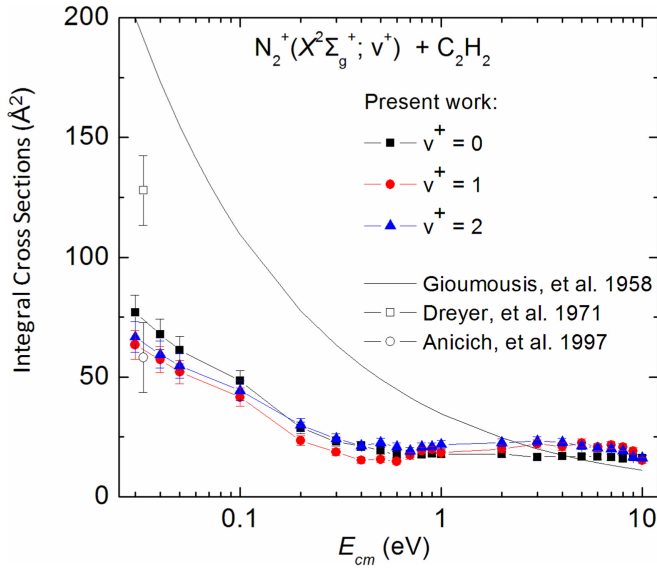


Figure 4. Comparison of the overall absolute integral cross sections or the sum $\sigma_{\text{CT}}(v^+) + \sigma_{\text{HT}}(v^+)$, for $v^+ = 0, 1$, and 2 , observed in the E_{cm} range of 0.03–10.00 eV. The results reported previously in Dreyer & Perner (1971) and Anicich & McEwan (1997) are shown as open squares and circles, respectively. The prediction (black curve) based on the LGS model (Gioumouis & Stevenson 1958) is also included.

rate coefficients (k_r) of previous studies (Dreyer & Perner 1971) are converted to integral cross sections (σ) by the relation $k_r = \sigma \langle v \rangle$, where $\langle v \rangle$ are the average velocity for the ion–molecule collisions that can be determined by the E_{cm} value using the formula $E_{\text{cm}} = \frac{1}{2} \mu \langle v \rangle^2$, where μ is the reduced mass for the N_2^+ and C_2H_2 collision system. Conversely, the

absolute integral cross section reported by the present work can be converted into the reaction rate coefficient. As shown in Figure 4, the result of Anicich et al. is consistent with that obtained in this experiment, while the experimental result of Dreyer et al. is higher than our results by about a factor of 2. The overall cross section curves for $v^+ = 0, 1$, and 2 plotted in Figure 4 clearly confirm the observation of the state-selected CT and HT cross sections of Figures 3(a) and (b) that the overall reactivity of N_2^+ is enhanced for vibrational excitations to $v^+ = 1$ and 2 states at higher $E_{\text{cm}} > 0.6$ eV and is inhibited at lower $E_{\text{cm}} < 0.2$ eV, comparing with that of the $v^+ = 0$ state.

The theoretical prediction (black line curve) based on the LGS model (Gioumouis & Stevenson 1958) is also shown in Figure 4. In the frame of the LGS model, the integral cross section is calculated by the formula

$$\sigma = \frac{2\pi e}{\langle v \rangle} \left(\frac{\alpha}{\mu} \right), \quad (4)$$

where e is the electron charge, $\alpha (= 4.24 \times 10^{-24} \text{ cm}^3)$ (Dreyer & Perner 1971) is the polarizability of C_2H_2 , μ is the reduced mass for the ion–molecule reaction system, and $\langle v \rangle$ is the average collision velocity that can be estimated from the corresponding E_{cm} value. At higher $E_{\text{cm}} \geq 2.00$ eV, the absolute integral cross sections measured in the present study are close to the prediction from the LGS model. However, large discrepancies are observed at the lower collision energy region of $E_{\text{cm}} < 2.00$ eV, and the prediction becomes nearly three times higher than the experimental measurements as the E_{cm} approaches thermal energies. The larger discrepancy at lower E_{cm} values, especially near thermal energies, indicates that the LGS model has oversimplified the reaction dynamics of reactions (2.1) and (2.2).

Product branching ratios. The branching ratios of the CT and HT channels for the $v^+ = 0, 1$, and 2 vibrational states have been obtained in the kinetic energy range $E_{\text{cm}} = 0.03$ –10.00 eV by comparing the measured intensities of the corresponding product C_2H_2^+ and N_2H^+ ions. These branching ratios are listed in Table 2. For all three vibrational states, the dominant product ion switches from C_2H_2^+ to N_2H^+ as the E_{cm} is increased from 0.03 to 10.00 eV.

For the reaction of $\text{N}_2^+(v^+)$ ions prepared in the $v^+ = 0$ vibrational state, the branching ratios for product C_2H_2^+ are found to be $\geq 95\%$ at $E_{\text{cm}} \approx 0.03$ eV. The observed trend of the branching ratios also suggests that the branching ratio of product N_2H^+ would further decrease at E_{cm} values below 30 meV. This observation is consistent with the results of previous studies that the formation of product N_2H^+ is negligibly small and the CT channel is the overwhelmingly dominant channel at thermal energies. Since the branching ratio for C_2H_2^+ decreases and that for N_2H^+ increases as E_{cm} is increased, the branching ratios of C_2H_2^+ and N_2H^+ become identical at $E_{\text{cm}} \approx 3.00$ eV. In the range of $E_{\text{cm}} = 3.00$ –10.00 eV, the branching ratio for N_2H^+ ions surpasses that for C_2H_2^+ ions as the dominant product ion formed by the ion–molecule reaction of $\text{N}_2^+(v^+ = 0) + \text{C}_2\text{H}_2$.

Similar trends for the product branching ratios are observed for the excited reactant $\text{N}_2^+(v^+ = 1$ and $2)$ vibrational states. In general, the branching ratios of product C_2H_2^+ ions formed in the reactions of the excited $\text{N}_2^+(v^+ = 1$ and $2)$ states are larger than those of the $\text{N}_2^+(v^+ = 0)$ ground state at the corresponding E_{cm} values. The detailed product branching ratios obtained for

Table 2
Product Branching Ratios of the CT and HT Channels of the Vibrationally State-selected Ion–Molecule Reaction
 $\text{N}_2^+(X^2\Sigma_g^+; v^+ = 0-2) + \text{C}_2\text{H}_2$ Measured in the E_{cm} Range of 0.03–10.00 eV

$E_{\text{cm}}(\text{eV})$	$v^+ = 0$		$v^+ = 1$		$v^+ = 2$	
	C_2H_2^+	N_2H^+	C_2H_2^+	N_2H^+	C_2H_2^+	N_2H^+
0.03	0.95 ± 0.01	0.05 ± 0.01	0.96 ± 0.01	0.04 ± 0.01	0.95 ± 0.01	0.05 ± 0.01
0.04	0.94 ± 0.01	0.06 ± 0.01	0.95 ± 0.01	0.05 ± 0.01	0.94 ± 0.01	0.06 ± 0.01
0.05	0.94 ± 0.01	0.06 ± 0.01	0.94 ± 0.01	0.06 ± 0.01	0.94 ± 0.01	0.06 ± 0.01
0.10	0.91 ± 0.02	0.09 ± 0.02	0.92 ± 0.01	0.08 ± 0.01	0.93 ± 0.01	0.07 ± 0.01
0.20	0.85 ± 0.03	0.15 ± 0.03	0.84 ± 0.03	0.16 ± 0.03	0.89 ± 0.02	0.11 ± 0.02
0.30	0.80 ± 0.03	0.20 ± 0.03	0.81 ± 0.03	0.19 ± 0.03	0.85 ± 0.03	0.15 ± 0.03
0.40	0.78 ± 0.03	0.22 ± 0.03	0.76 ± 0.04	0.24 ± 0.04	0.84 ± 0.03	0.16 ± 0.03
0.50	0.73 ± 0.04	0.27 ± 0.04	0.74 ± 0.04	0.26 ± 0.04	0.82 ± 0.03	0.18 ± 0.03
0.60	0.72 ± 0.04	0.28 ± 0.04	0.66 ± 0.04	0.34 ± 0.04	0.77 ± 0.04	0.23 ± 0.04
0.70	0.64 ± 0.05	0.35 ± 0.05	0.65 ± 0.05	0.35 ± 0.05	0.73 ± 0.04	0.27 ± 0.04
0.80	0.61 ± 0.05	0.39 ± 0.05	0.62 ± 0.05	0.38 ± 0.05	0.73 ± 0.04	0.27 ± 0.04
0.90	0.57 ± 0.05	0.43 ± 0.05	0.59 ± 0.05	0.41 ± 0.05	0.70 ± 0.04	0.30 ± 0.04
1.00	0.56 ± 0.05	0.44 ± 0.05	0.55 ± 0.05	0.45 ± 0.05	0.68 ± 0.04	0.32 ± 0.04
2.00	0.52 ± 0.05	0.48 ± 0.05	0.58 ± 0.05	0.42 ± 0.05	0.64 ± 0.05	0.36 ± 0.05
3.00	0.50 ± 0.05	0.50 ± 0.05	0.57 ± 0.05	0.43 ± 0.05	0.63 ± 0.05	0.37 ± 0.05
4.00	0.48 ± 0.05	0.52 ± 0.05	0.52 ± 0.05	0.48 ± 0.05	0.61 ± 0.05	0.39 ± 0.05
5.00	0.48 ± 0.05	0.52 ± 0.05	0.55 ± 0.05	0.45 ± 0.05	0.56 ± 0.05	0.44 ± 0.05
6.00	0.39 ± 0.05	0.61 ± 0.05	0.49 ± 0.05	0.51 ± 0.05	0.52 ± 0.05	0.48 ± 0.05
7.00	0.33 ± 0.04	0.67 ± 0.04	0.48 ± 0.05	0.52 ± 0.05	0.49 ± 0.05	0.51 ± 0.05
8.00	0.31 ± 0.04	0.69 ± 0.04	0.48 ± 0.05	0.52 ± 0.05	0.46 ± 0.05	0.54 ± 0.05
9.00	0.29 ± 0.04	0.71 ± 0.04	0.40 ± 0.05	0.60 ± 0.05	0.37 ± 0.05	0.63 ± 0.05
10.00	0.19 ± 0.03	0.81 ± 0.03	0.29 ± 0.04	0.71 ± 0.04	0.31 ± 0.04	0.69 ± 0.04

Note. The uncertainties are based on standard deviations observed in at least six independent measurements.

the vibrationally selected ion–molecule reaction system $\text{N}_2^+(X^2\Sigma_g^+; v^+ = 0-2) + \text{C}_2\text{H}_2$ at a wide range of E_{cm} from 0.03 to 10.00 eV as listed in Table 2 are expected to be valuable in contributing to the experimental database for modeling of the atmospheres of relevant planets or satellites, such as Saturn’s largest moon, Titan.

4. CONCLUSIONS

The vibrationally state-selected ion–molecule reaction system of $\text{N}_2^+(X^2\Sigma_g^+; v^+ = 0-2) + \text{C}_2\text{H}_2$ has been studied by combining the high-resolution VUV-PFI-PI technique and the DQDO mass spectrometer developed in our laboratory. Detailed absolute integral cross sections and branching ratios for the CT and HT channels have been measured covering an unprecedentedly wide E_{cm} range of 0.03–10.00 eV. The integral cross section for the CT channel is found to decrease with the increase of the kinetic energy, but the opposite trend is observed of that for the HT channel. The E_{cm} dependence of the CT channel observed is consistent with a long-range exothermic CT mechanism, whereas that for the HT channel is partially enhanced by collision energies. The vibrationally selected cross-section measurements for both the CT and HT channels reveal only marginal vibrational effects. The comparison of the sum of $\sigma_{\text{CT}}(v^+) + \sigma_{\text{HT}}(v^+)$, for $v^+ = 0, 1$, and 2, shows that the reactivity of $\text{N}_2^+(v^+)$ toward C_2H_2 is slightly inhibited by vibrational excitation at low $E_{\text{cm}} < 0.60$ eV, whereas a slight enhancement is observed at high $E_{\text{cm}} > 1.00$ eV. Both the integral cross sections and the branch ratios obtained in the present work are valuable for benchmarking state-of-the-art theoretical calculations and for the modeling of the chemical composition of Titan’s atmosphere.

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