

Laboratory spectroscopic studies of the collisions between slow H^+ , H_2^+ , H_3^+ ions and molecular nitrogen

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Received 20 April 2011 / Accepted 7 August 2011

ABSTRACT

Luminescence in the 275–470 nm spectral region was observed in the collisions of H^+ , H_2^+ , and H_3^+ with N_2 in the 10–1000 eV projectile energy range. For all the systems, a luminescent charge exchange leads to the electronically excited states of $N_2^+(B^2\Sigma_u)$ and $N_2(C^2\Pi_u, G^2\Delta_g)$. Computer simulation of the spectra was used to estimate relative cross sections for the reactions, as well as the temperatures corresponding to population distributions of vibrational and rotational levels of the products. The vibrational temperatures of the products for the $H_2^+ + N_2$ and $H_3^+ + N_2$ collision systems are found to be changing significantly with the projectile velocity, increasing from 1500 K at the lowest projectile velocities ($\leq 50 \text{ km s}^{-1}$) and going through a maximum (15 000 K) at about 80 km s^{-1} , to decrease rapidly with increasing velocity, down to 3000 K. The $H^+ + N_2$ collision system, however, does not show a similar increase in temperature. The increase in vibrational temperature indicates that, for velocities in the 50–1000 km s^{-1} range, the charge transfer process is the non-Franck-Condon type, a model that assumes a change in the internuclear distance of target molecule by the incident ion before electron capture occurs. This vibrational temperature dependency could be used to infer the ion velocity producing the observed emission of N_2^+ . Also we found no evidence of any formation of excited NH molecules in these reactions.

Key words. astrochemistry – ISM: abundances – ISM: molecules – methods: laboratory

1. Introduction

The interaction of the stellar wind and interstellar medium is of strong interest to cosmochemistry. Nitrogen is the fifth most abundant element in the Solar System (Arnett 1996) and the seventh in Milky Way Galaxy (Crowell 2000). According to interstellar chemistry models, nitrogen should mainly be in a molecular form (N_2). Nevertheless, it has not have been observed directly for a long time (neither in absorption nor emission). The first direct observation of molecular nitrogen in the interstellar media was achieved at far-ultraviolet absorption towards the HD 124314 star with the help of the Far Ultraviolet Spectroscopic Explorer (FUSE) (Knauth et al. 2004).

Before that, ionized molecular nitrogen has been observed in the emission of bright comets approaching the Sun. Comets are important, because they could contain information about an early protosolar cloud. The N_2^+ spectra were observed spectroscopically in comet Halley (Wyckoff & Theobald 1989) or Scorichenko-George (1989e₁) (Churyumov & Chorny 1992). There are comets where no N_2^+ has been detected: comet C/2002 C1 (Ikeya-Zhang) (Cochran 2002), or comets 122P/1995 S1 (deVico) and C/1995 O1 (Hale-Bopp) (Cochran et al. 2000). From spectroscopic observations the N_2^+/CO^+ ratio or upper limit for this ratio was estimated as very low. The investigations of the excitation conditions in comets leading to the observed N_2^+ bands could be useful for more accurate determination of the N_2 abundance. Recently, the N_2^+ emission was observed in a bright meteor Leonid fireball (Shinsuke et al. 2005).

Stars emit a constant stream of particles (Lamers & Cassinelli 1999), mainly protons (H^+) and electrons, along with other elements with abundances a few orders of magnitude smaller (Geiss et al. 1994). Gruntman (1996) has analyzed the

possibility of forming the H_2^+ ion flux; the solar wind ionize and pickup encountered in heliosphere or in local interstellar medium H_2 molecule, or due to outgassing of interplanetary dust.

The stellar wind can be gentle (as for the Sun) and difficult to detect from the Earth. However, the intensity and dynamics vary significantly between different stars. A star like the Sun exhibits a stellar wind with particles velocities between 200 km s^{-1} from solar surfaces and 700 km s^{-1} from coronal holes (Böhm-Vitense 1989). Cooler stars, typically red giants, produce winds with lower velocities (about 20 km s^{-1}), while hot stars exhibit much stronger winds with speeds up to 2000 km s^{-1} (Lamers & Cassinelli 1999). Also the stellar wind changes during the life of a star.

The energetic protons in the stellar wind interact with the molecules encountered (in interstellar cloud, comet entourage, or atmosphere) and are transformed into excited neutral hydrogen atoms by charge exchange collisions with molecular cloud, and they also produce various excited components.

In this paper, the collisions of the H^+ , H_2^+ , and H_3^+ hydrogen ions with molecular nitrogen N_2 are studied at collision energies below 1000 eV. Because N_2 in the excited states may have enhanced chemical reactivity, as well as characteristic radiation, these reactions are important because of their strong role in the synthesis of molecular species in dense interstellar media. The relevant velocities of the charged particles in this paper are similar to the one ejected by the Sun, in the range of 30 km s^{-1} to 430 km s^{-1} .

Besides Earth, there are only three objects in the Solar System that contain molecular nitrogen in their atmosphere. Titan, the largest moon of Saturn, Triton (the largest moon of the planet Neptune) and Pluto have atmospheres that are mainly

composed of molecular nitrogen. The solar wind may cause the auroral emission, leading to a spectacular light phenomenon. These systems (H^+ , H_2^+ , $H_3^+ + N_2$) have been studied in the past, but only a few of them present emission spectra and cross section data below the 1000 eV collision energy range.

Hydrogen ions interacting with N_2 molecules have been studied spectroscopically by observing hydrogen radiation of Balmer series H_β (486.1 nm) in the 3–10 keV energy range (Lee & Lin 2002) and H_α (656.3 nm) emission in the 3–100 keV energy range (Yousif et al. 1986). The absolute emission cross sections for the H_β and H_α lines are around 10^{-17} cm².

Using the time-of-flight technique, Luna et al. (2003) have measured electron capture and ionization cross sections for the incident of H^+ on N_2 in the 10–100 keV energy range. The values obtained are close to 10^{-16} cm². With the same technique Hasan (2005) measured the total cross sections for collisions of H_2^+ ions with an N_2 molecule in the 700–2000 eV energy range, obtaining values on the order of 10^{-16} cm². Using a mass-spectrometric technique Browning & Gilbody (1968) also measured cross section for formation of various ions in the $H^+ + N_2$ collision in the 5–45 keV energy range. From their studies it follows that electron capture process dominates, and the N_2^+ production is 2 to 3 orders of magnitude more efficient than N_2^{2+} or than dissociation into N^+ ions.

Lee & Suen (1998) spectroscopically studied the $N_2^+(B-X)$ first negative system excitation in the uv-visible spectrum between 300 and 450 nm that is induced by bombardment of molecular nitrogen by the H^+ , H_2^+ and H_3^+ hydrogen ions in the 2–10 keV energy range. They measured the cross section for the emission of the (0, 0) band at 391.4 nm and (0, 1) band at 427.8 nm of the N_2^+ first negative system. Additionally, the $I(0, 0)/I(0, 1)$ branching ratio of the $N_2^+(B-X)$ was measured as a function of ion energy. The emission cross sections for low-energy (63–2500 eV) H^+ and H impacting on N_2 have been measured by Van Zyl et al. (1983).

Interaction of molecular nitrogen with other ions was also investigated using spectroscopic techniques. Ottinger & Simonis (1978) studied the charge transfer of C^+ , N^+ , and O^+ ions in metastable and ground states with N_2 at 1000 eV energy. Bearman et al. (1976) measured the cross section for charge transfer collision between the He^+ , He_2^+ ions, and N_2 at 11 eV energy. In both papers the high resolution spectra show changes in vibrational state distribution. The light emission in the 200 to 500 nm range and a cross section at 10–20 eV_{CM} of the $Ar^{2+} + N_2$ reaction have been measured in Neuschäfer et al. (1979).

This paper presents the results of collisional excitation of the nitrogen molecule in the reactions of the H^+ , H_2^+ and H_3^+ with N_2 below 1000 eV energy in single-collision conditions. The luminescence from the UV to the visible light (270–470 nm) was obtained at various energies. Experimental results are supported by the computer simulations, which allow identifying the products arisen in the reactions studied and moreover their relative abundances and population distributions to be determined over rotational and vibrational levels.

2. Experiment

The experiment was performed in an ion beam – gas arrangement with the apparatus that is described in detail in Kowalski et al. (2004b). Basically, it is composed of an ion source, a mass spectrometer, a reaction cell, and an optical spectrometer.

Hydrogen ions were produced in a Colutron-type source, operating on H_2 gas at a pressure of ~100 Pa. The anode-to-cathode

voltage in a source was set to 100 V, and the discharge current was 0.5 A. These conditions of the source assured the highest intensity of the ion beam. Subsequently, hydrogen ions were extracted by a 1000 V potential to the primary mass spectrometer. Before entering the collision cell, ions were decelerated to the desired laboratory energy.

Light produced in the collision region was recorded with a 1024 channel “Mepsicron” detector connected to a McPherson 218 spectrograph, which was equipped with a 300 l/mm grating blazed at 500 nm. Each measurement simultaneously covered a spectral range of 200 nm. The spectral resolution was 1.5 nm *FWHM*. For an accurate identification of spectra components and determination of the population distribution over the rotational levels, high-resolution spectra were taken with a 1200 l/mm grating blazed at 250 nm, and the resolution was 0.25 nm *FWHM*. The pressure of the target gas was 15 mTr, as determined with a Barocel capacitance manometer.

The ion current measured behind the reaction cell during the measurements was approximately 0.2 nA at 50 eV, about 6 nA at 1000 eV for H^+ , and 50 nA for H_2^+ , H_3^+ at 1000 eV. The chemiluminescence signal (integrated over all 1024 detector channels) was between 3 and 700 counts per second, depending on the current of the hydrogen ion beam. The detector dark count rate integrated over all 1024 channels was 2 cts/s. The spectra were taken at several different beam energies, ranging from 10 eV_{LAB} (9.7, 9.3, and 9.0 eV_{CM} for the H^+ , H_2^+ , and H_3^+ ions, respectively) to 1000 eV_{LAB} (966, 933, and 903 eV_{CM} for the H^+ , H_2^+ , and H_3^+ ions, respectively).

3. Results

Examples of the recorded luminescence spectra for the H^+ , H_2^+ , and $H_3^+ + N_2$ collisions at $E_{LAB} = 1000$ eV, 400 eV, 100 eV, 50 eV, and 10 eV are presented in Fig. 1. The light accumulation times varied from 10 to 120 min per spectrum, depending on the signal intensity. All spectra were smoothed over seven channels.

The energy dependence of the relative luminescence cross sections for the H^+ , H_2^+ , and $H_3^+ + N_2$ collision systems are presented in Fig. 2. Only the cross sections from $E_{LAB} = 1000$ eV down to 50 eV are presented, because the uncertainties are very high for lower energies.

The various complex processes in the reactions of hydrogen ions with the N_2 molecule could result in the formation of different products (i.e.: H_2 , N_2 , N_2^+ , NH , NH^+ , HN_2^+ and atomic H , N , N^+) in diverse excited states, as well in the ground state. Reaction products in the ground or metastable states are not detectable in our experiment. However, excited products emitting in the UV-Vis range between 275 nm and 470 nm can be recorded.

To correctly identify products in the complex spectra, computer simulations are required (Pranszke et al. 2011). From simulations we have identified three main molecular emission bands in the observed region: $N_2^+(B^2\Sigma_u - X^2\Sigma_g)$, $N_2(C^3\Pi_u - B^3\Pi_g)$ and $N_2(G^3\Delta_g - W^3\Delta_u)$. We also found atomic emission of the hydrogen line of Balmer series, namely H_γ (434.1 nm).

An example of simulations for the $H_2^+ + N_2$ reaction at 400 eV is shown in Fig. 3a, where the experimental spectrum and the best fit of the computer generated spectrum composed of contributions from molecular emitters detected in the experiment are presented. The final contour is a convolution of the following contours: $N_2^+(B-X)$ transition presented in Fig. 3b, $N_2(C-B)$ transition presented in Fig. 3c, and $N_2(G-W)$ shown in Fig. 3d,

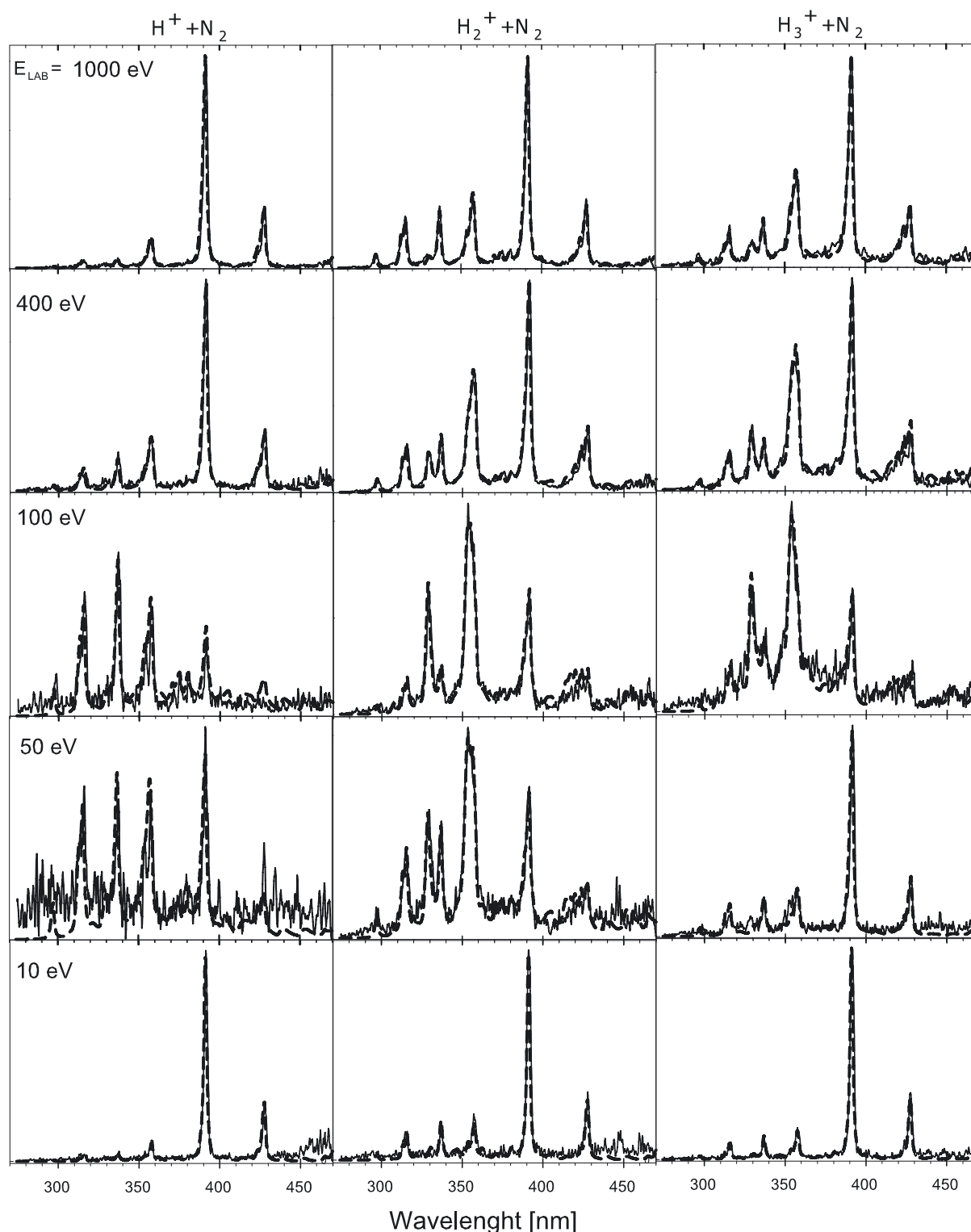


Fig. 1. Selected luminescence spectra for the $\text{H}^+ + \text{N}_2$, $\text{H}_2^+ + \text{N}_2$, and $\text{H}_3^+ + \text{N}_2$ systems at various collision energies, as indicated. The thick dashed contours are computer simulations. The spectral resolution is 1.5 nm *FWHM*.

with weights proportional to the intensity of each feature. The $\text{N}_2^+(\text{B}^2\Sigma_u - \text{X}^2\Sigma_g)$ and $\text{N}_2(\text{C}^3\Pi_u - \text{B}^3\Pi_g)$ systems have clearly visible peak components indicated in Fig. 3b–d.

To calculate the synthetic spectra for the $\text{N}_2^+(\text{B}^2\Sigma_u - \text{X}^2\Sigma_g)$, $\text{N}_2(\text{C}^3\Pi_u - \text{B}^3\Pi_g)$, and $\text{N}_2(\text{G}^3\Delta_g - \text{W}^3\Delta_u)$ transitions, we used the formulas for rotational energy levels from Herzberg (1965).

The set of data for molecular constants for $\text{N}_2^+(\text{B-X})$ were taken from Klynning & Pages (1982), for $\text{N}_2(\text{C-B})$ from Tyte & Nicholls (1964) and for $\text{N}_2(\text{G-W})$ from Bachmann et al. (1993).

The number of vibrational and rotational levels is limited by the dissociation energy for a given electronic state and in some cases by the predissociation of a molecule. This is the case of

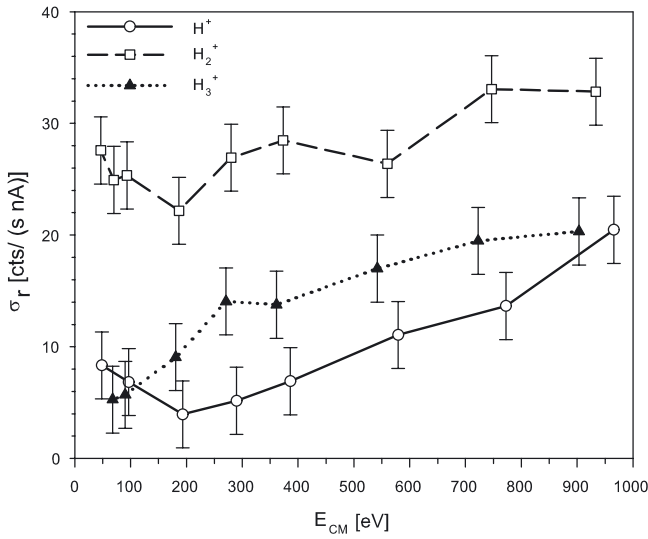


Fig. 2. Excitation functions for $\text{H}^+ + \text{N}_2$, $\text{H}_2^+ + \text{N}_2$, and $\text{H}_3^+ + \text{N}_2$.

$\text{N}_2(\text{C}^3\Pi_u - \text{B}^3\Pi_g)$ band, where the predissociation of the $\text{C}^3\Pi_u$ state to the $^4\text{S} + ^2\text{D}$ dissociation limit precludes all bands above $v' > 4$, while $\text{B}^3\Pi_g$ is predissociated above $v' > 12$ to the $^4\text{S} + ^4\text{S}$ dissociation limit (Tyte & Nicholls 1964). For the $\text{N}_2^+(\text{B}^2\Sigma_u - \text{X}^2\Sigma_g)$ system, the highest vibrational level values ever observed are $v' = 29$ and $v'' = 23$ for the B and X states, respectively.

The symmetry and multiplicity of electronic states are taken into account. For the N_2^+ electronic transitions, the $\text{B}^2\Sigma_u$ and $\text{X}^2\Sigma_g$ states are assumed to be Hund's case (b) (Herzberg 1965). For the N_2 molecule, the coupling type for the $\text{B}^3\Pi_g$ and $\text{C}^3\Pi_u$ states are Hund's case (a) for lower J values and Hund's case (b) for higher J values (Herzberg 1965).

In the next step, the procedure determines the relative intensity for each component. We let $n = (v', J')$ and $m = (v, J)$ be two molecular states. The intensity of the transition is a product of: transition wavelength λ^{-1} , the Einstein coefficient proportional to λ^{-3} , the Franck-Condon factors (FCF) describing the vibrational excitation, the Hönl-London factors (HLF) that describe the rotational line strength, and the distribution of populations in rotational P_r and vibrational P_v levels:

$$I_{n \rightarrow m}(v', J', v, J) = N_n \frac{hc^2}{\lambda_{nm}} A_{nm} \text{FCF}(v', v) \frac{\text{HLF}(J', J)}{(2J' + 1)} \times P_v(T_{\text{vib}}, v') P_r(T_{\text{rot}}, v', J'), \quad (1)$$

where N_n is the number of emitting molecules, λ_{nm} the transition wavelength, $A_{nm} = (64\pi^4)/(3h\lambda_{nm}^3)|R^{nm}|^2$ is the Einstein coefficient, $\text{FCF}(v', v)$ the Franck-Condon factor, $\text{HL}(J', J)$ the Hönl-London Factors and P_{vib} and P_{rot} are the vibrational and rotational population distributions.

For the $\text{N}_2^+(\text{B-X})$ system, the FCF factors were taken from Tyte & Nicholls (1965). The FCF for the $\text{N}_2(\text{C-B})$ second positive system were taken from Tyte & Nicholls (1964), and Bachman et al. (1993) for the $\text{N}_2(\text{G-W})$ system.

The Hönl-London factors for $\text{N}_2^+(\text{B}^2\Sigma_u - \text{X}^2\Sigma_g)$ transition were taken from Mulliken (1931). For the triplet $\text{N}_2(\text{C}^3\Pi_u - \text{B}^3\Pi_g)$ transition, the appropriate HLF factors were taken from Schadee (1964) and Herzberg (1965) for the $\text{N}_2(\text{G}^3\Delta_g - \text{W}^3\Delta_u)$ transition.

For all collision systems, the relative rotational and vibrational populations were assumed to be given by the Boltzmann

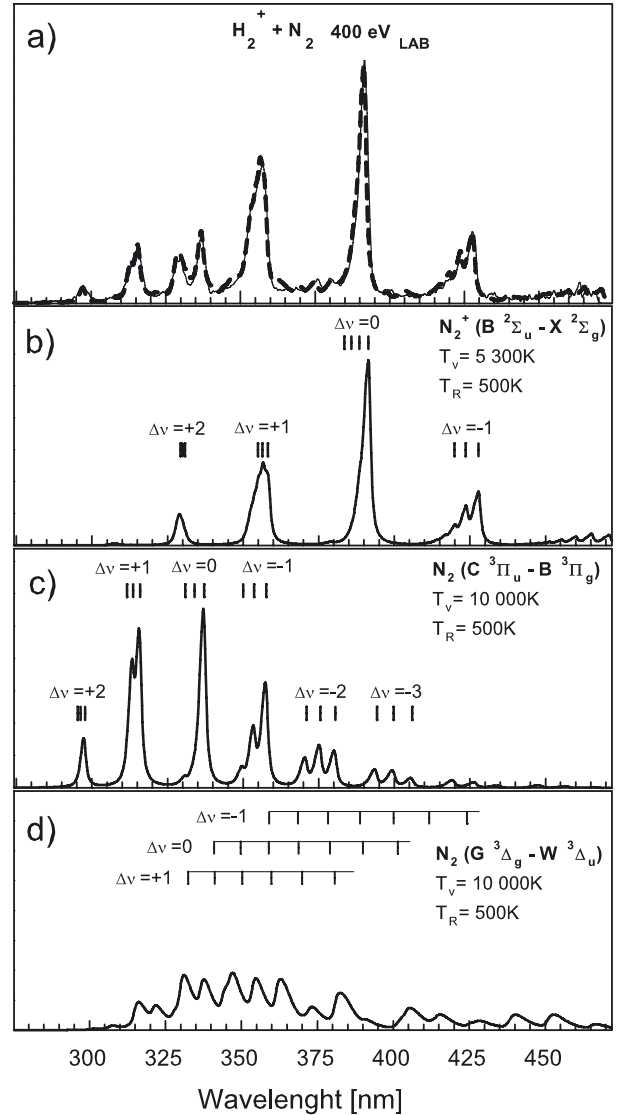


Fig. 3. a) Experimental spectrum (solid line) compared to the simulated one (dashed line) in the $\text{H}_2^+ + \text{N}_2$ collision at the energy 400 eV. b)–d) show contributions from molecular emitters detected in the experiment.

distribution described by only one parameter - the temperature,

$$P_v(T_v, v') = e^{-\Delta E_v(v', 0)/(k_B T_v)} \quad (2)$$

$$P_r(T_r, v', J') = (2J' + 1) e^{-\Delta E_J(J', 0)/(k_B T_r)}, \quad (3)$$

where $\Delta E_v(v', 0)$ is the energy difference between the vibrational v' and $v' = 0$ levels, $\Delta E_J(J', 0)$ is energy difference between the rotational J' and $J' = 0$ levels, and k_B is the Boltzmann constant.

A vibrational temperature provides information on a vibrational excited species, and the relative rates of energy exchange processes. Only at certain energies do we need to modify vibrational populations distribution to slightly improve the quality of fitting of synthetic spectra to experimental. In the $\text{H}_2^+ + \text{N}_2$ collision system at $E_{\text{LAB}} = 100$ eV, $v' \leq 1$ vibrational levels were depopulated by a factor 0.8. For the $\text{H}_3^+ + \text{N}_2$, populations of $v' \leq 2$ vibrational levels were reduced by a factor of 0.6 at $E_{\text{LAB}} = 75, 100$ and 200 eV energies.

For each band a convolution of all transitions was made, calculated with the assumed Lorentzian intensity distribution

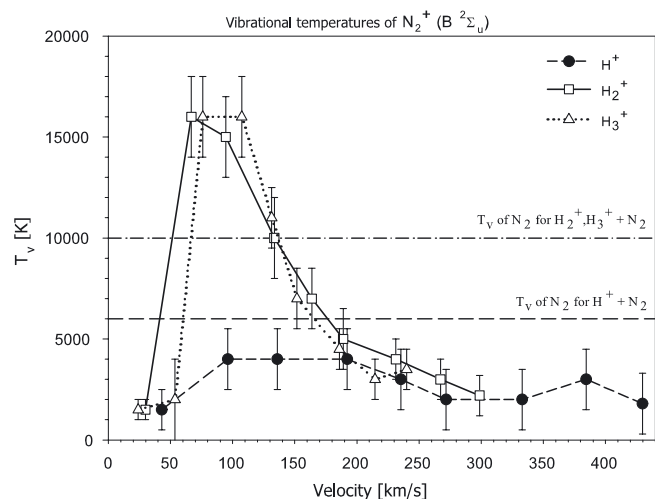


Fig. 4. Vibrational temperatures of the $N_2^+(B)$ product determined for the $H^+ + N_2$, $H_2^+ + N_2$, and $H_3^+ + N_2$ collision systems.

function for each line. Finally, all simulated molecular bands were combined together into one spectrum, and the relative fractions of contributions were estimated.

4. Discussion

By comparing of the series of spectra presented in Fig. 1, one can notice the following features. In all collision systems, the $N_2^+(B-X)$ ($\Delta v = 0$) band at 391 nm dominates in the spectra for high energies (above $E_{CM} = 400$ eV) and for energies below 25 eV. For intermediate energies (between 50 and 400 eV), the intensity of the 391 nm band decreases, while the band at 358 nm (composed of $\Delta v = +1$ of $N_2^+(B-X)$ and $\Delta v = -1$ of $N_2(C-B)$) increases.

This can be explained by a significant increase in the vibrational temperature. From Fig. 4 where we present the vibrational temperatures of $N_2^+(B^2\Sigma_u)$ and $N_2(C^3\Pi_u)$ as a function of projectile velocity, we see that the physical processes present in collision of H_2^+ or H_3^+ ions with the N_2 molecule depend on projectile velocity and, in a certain velocity range lead to very high vibrational excitation. The temperature for velocities over 250 km s^{-1} is about 3000 K, while for velocities near 75 km s^{-1} , the temperature rises to 15000 K. In contrast, the $H^+ + N_2$ collision system does not show this effect; i.e. for all projectile velocities the vibrational temperature is constant and equal to $T_{vib} = (3000 \pm 1500)$ K. For all systems, at velocities below 60 km s^{-1} , the vibrational temperature decreases rapidly down to (1500 ± 500) K.

The measurements of the relative band intensities of the $\Delta v = -1$ sequence of the $N_2^+(B-X)$ system at 427.8 nm excited by H^+ and H_2^+ ion beams in a wide velocity range (from 60 up to 2180 km s^{-1}); Moore & Doering (1969); Birely (1974) have shown the significant shifts in vibrational distribution of N_2^+ to higher vibrational levels for velocities below 1000 km s^{-1} . On the other hand, the relative band intensities of the $N_2^+(B-X)$ system excited by thermic ions of helium and argon in an afterglow at 400 K gas temperature Robertson (1966) did not show any enhancement of population distributions.

In this paper, for projectile velocities between $70\text{--}200 \text{ km s}^{-1}$ (50–400 eV) for H_2^+ , $H_3^+ + N_2$ collision systems we also observed the shifts of vibrational distribution in terms of increment of the

vibrational temperature. To check our results with the help of our computer program, we determined the vibrational temperatures from high-resolution spectra of the N_2^+ first negative system $\Delta v = -1$ sequence (see Fig. 1 in Moore & Doering 1969) excited by 0.3 keV, 1 keV, 3 keV and 10 keV- H_2^+ ions, the obtained values are 12000 K, 3000 K, 2000 K, and 1500 K, respectively, with about 20% relative uncertainty. These values agree with results obtained in our experiment.

The relative band intensities (the product of relative population and FC factors, Moore & Doering 1969; Birely 1974) or the vibrational temperatures determined in this paper are based on using the Franck-Condon factors determined for electronic transitions of isolated N_2 and N_2^+ molecules. But for the ion-molecule collision complex, this factor could be different and depend on the velocity of the perturbing ion.

From results of the relative band intensity measurements or vibrational temperature, we see that, for very low velocities (below 50 km s^{-1}) and for very high velocities ($>1000 \text{ km s}^{-1}$), the Franck-Condon model (assuming vertical ionization of $N_2(X^1\Sigma_g^+, v = 0)$ to N_2^+) satisfactory describes the observed spectra and that the vibrational temperature of the N_2^+ molecule droops to same given value (for instance <1500 K for $H_2^+ + N_2$). However, for velocities $50\text{--}1000 \text{ km s}^{-1}$ the Franck-Condon model is inadequate.

However, the $H^+ + N_2$ system differs, since we did not observe a very enormous increase in the vibrational temperature. This contradicts some conclusions from the intensity ratio measurements of Moore & Doering (1969) that “*The vibrational excitation was found to be solely dependent on the projectile ion’s laboratory velocity and independent of its chemical identity*”. It appears that vibrational distribution depends on type of projectile.

Another feature is the increased intensity of the $N_2(C-B)$ bands ($\Delta v = +2$ at 297 nm, $\Delta v = +1$ at 316 nm and $\Delta v = 0$ at 337 nm) in the $H_2^+ + N_2$ and $H_3^+ + N_2$ collision systems. Once again these two cases differ from the $H^+ + N_2$ system, where the abundance of $N_2(C-B)$ is clearly smaller. Also the N_2^+/N_2 ratio changes with the projectile energy.

Furthermore, at energies in the 50–400 eV range a quasi-continuum appears in the 300–400 nm range. This feature was observed earlier for the Ne^+ (Brandt et al. 1973), He^+ (Simonis 1977) and Ar^{2+} (Neuschäfer et al. 1979) impact on N_2 at low energies. At first, this feature was tentatively assigned to the $N_2^+(B-X)$ tail bands (emission from high vibrational levels of $N_2^+(B)$); (Neuschäfer et al. 1979). However, high-resolution spectra presented in Fig. 5 do not support this. Here only $v' < 3$ band heads are visible. Later Simonis (1977) proposed that the charge transfer populates some high-lying electronic states of N_2^+ , from there cascading transitions to the ground state occur, emitting the quasi-continuum.

In our studies we propose another explanation. This quasi-continuum feature is an $N_2(G^3\Delta_g - W^3\Delta_u)$ band system discovered and investigated in Bachmann et al. (1993). From computer simulations of this band presented in Fig. 3d we can see the quasi-continuum shape of this transition. Additionally the very good agreement between experimental and computer-generated spectra (see Fig. 1) confirms our assumption. Another argument for this is that we have observed another electronically excited state of N_2 .

While the vibrational temperature for $N_2^+(B^2\Sigma_u)$ varies significantly with collision energy, it is constant at all energies for the N_2 states. For the $H^+ + N_2$ system $T_{vib} = (6000 \pm 2000)$ K and for the H_2^+ , $H_3^+ + N_2$ systems, $T_{vib} = (10000 \pm 2000)$ K.

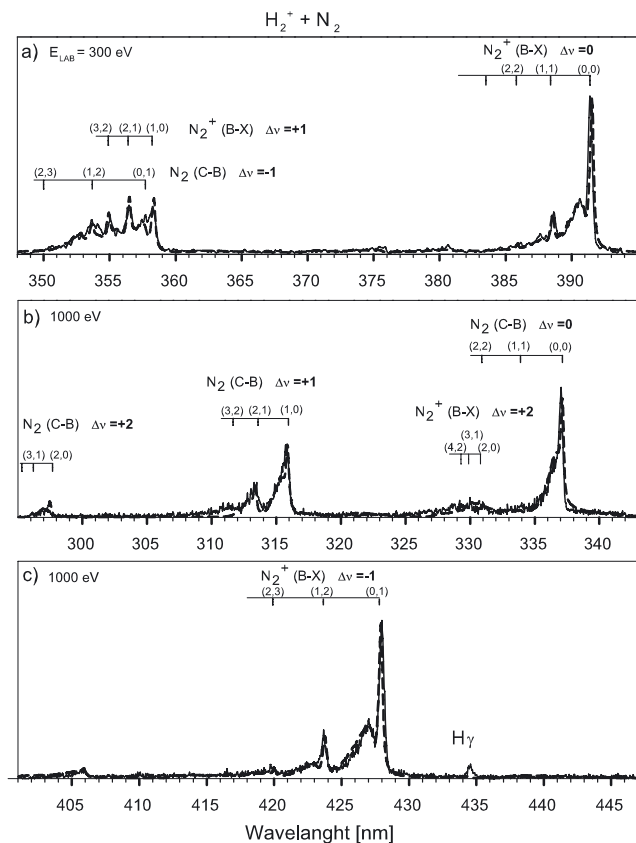


Fig. 5. Experimental spectra (solid line) compared to the simulated ones (dashed line) for the $\text{H}_2^+ + \text{N}_2$ collisions. Spectral resolution is 0.25 nm FWHM.

The products formed in all investigated collision systems were found to be in a non equilibrium state, and the rotational temperature appears to be independent of processes leading to enormous vibrational excitation. From high resolution spectra collected for all collision systems and at several energies (examples are presented in Fig. 5), we have estimated the rotational temperatures T_{rot} for the analyzed bands for which the simulated contour fits the experimental one satisfactorily. From these studies, we found that, for the 50–1000 eV energy range and for all collision systems, the rotational temperature is constant and is roughly equal to the gas kinetic temperature $T_{\text{rot}} = (500 \pm 300)$ K and slightly decreases to (200 ± 100) K for energies below 50 eV.

The total relative emission cross sections for the investigated collision systems are presented in Fig. 2. The experimental uncertainties are mean standard deviations from 3 up to 14 independent measurements at given energy. For the H^+ , $\text{H}_3^+ + \text{N}_2$ collision systems, the cross section increases almost three times through the 50–1000 eV energy range. In contrast, the cross section for the $\text{H}_2^+ + \text{N}_2$ collision system is higher than H^+ , $\text{H}_3^+ + \text{N}_2$ systems, and practically does not change through the entire investigated energy range.

With the help of computer simulations we were able to determine the relative abundances of different molecular bands in overall spectra for each energy. Van Zyl et al. (1983) measured N_2^+ ($\Delta v = -1$ at 427.8 nm) absolute emission cross sections for H^+ impacting on N_2 in the 63–2000 eV energy range. These values can be used to calibrate our relative cross sections. The N_2^+ ($\Delta v = -1$ at 427.8 nm) band makes about 19% of all N_2^+ (B-X) spectra, thus the absolute cross section for N_2^+ (B) excitation from Van Zyl et al. (1983) was divided by 0.19. In this way, we

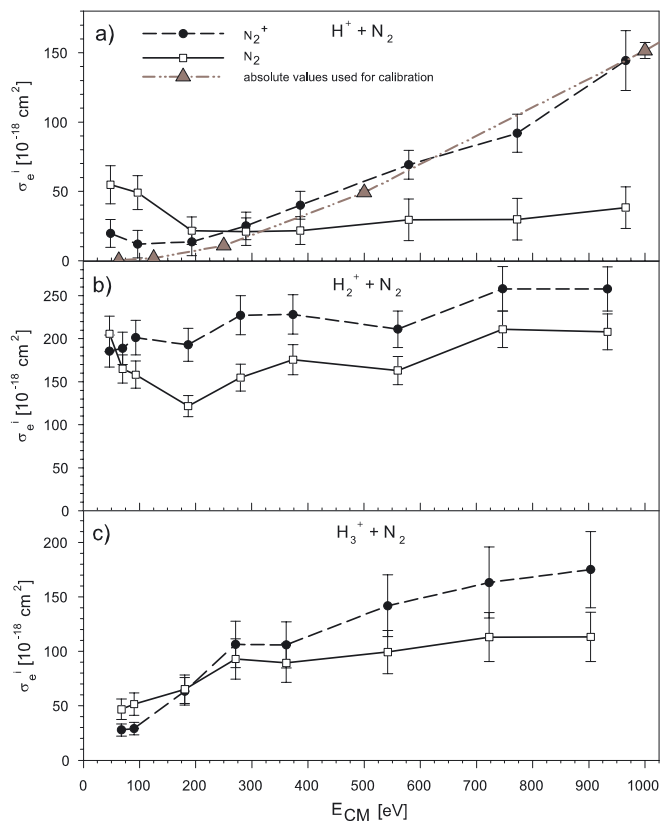


Fig. 6. Normalized absolute emission cross sections of identified products for a) $\text{H}^+ + \text{N}_2$, b) $\text{H}_2^+ + \text{N}_2$, c) $\text{H}_3^+ + \text{N}_2$ collision systems; \bullet - N_2^+ , \square - N_2 , \blacktriangle - data from Van Zyl et al. (1983).

found the multiplier converting our relative cross sections into the absolute values. The calibrated absolute cross sections of the identified products for the $\text{H}^+ + \text{N}_2$, $\text{H}_2^+ + \text{N}_2$, and $\text{H}_3^+ + \text{N}_2$ collision systems are presented in Fig. 6a–c. Here the energy – dependent luminescence cross section of N_2^+ (B-X) and sum of two observed N_2 bands are plotted together with the absolute cross sections for $\text{H}^+ + \text{N}_2$ collision system of Van Zyl et al. (1983).

Gao et al. (1990) report the measurements of differential and integral absolute cross sections for charge transfer in collisions of H^+ and He^+ with several molecules, including the N_2 at 0.5, 1.5, and 5.0 keV energies. Van Zyl et al. (1983) determined total emission cross section of the N_2^+ 427.8 nm band induced by the H^+ impact on N_2 at 500 eV energy and obtained a value of about $9.34 \times 10^{-18} \text{ cm}^2$. This band, at vibrational temperatures determined in this paper, makes about 19% of all N_2^+ (B-X) spectra. Using the total cross sections for electron capture at 500 eV ($2.5 \times 10^{-16} \text{ cm}^2$) obtained by Gao et al. (1990), we can estimate that the percentage of the total charge transfer reactions leading to the electronically excited state product is about 20%. Extrapolating Gao et al. (1990) values to 1000 eV and using the Van Zyl et al. (1983) emission cross section, we see that about 30% of collisions lead to excited products.

Combining the total cross sections for electron capture at 2000 eV ($5.03 \times 10^{-16} \text{ cm}^2$) measured in Hasan (2005) and the emission cross section of the N_2^+ 427.8 nm band induced by the H_2^+ impact on N_2 at 2000 eV energy ($7 \times 10^{-18} \text{ cm}^2$) determined in Lee & Suen (1998), the percentage of the total charge transfer reactions leading to the electronically excited state product is about 7%. Extrapolating results from Lee & Suen (1998) to 1000 eV and Hasan (2005) gives 4%.

But these percentages strongly disagree with the values obtained where taking the emission cross sections for $H_2^+ + N_2$ determined in present paper. For instance, using values of Hasan (2005) and the present result at 1000 eV energy, we obtain 65% of the collisions leading to excited products (two times higher than at the same energy in $H^+ + N_2$ collision), while it was only 4% for σ_e determined in Lee & Suen (1998). This discrepancy is a consequence of using by Lee & Suen (1998) values of (Sheridan & Clark 1965) for calibration, were procedures for absolute calibration of the photon detector used were not highly accurate Van Zyl et al. (1983). For calibration in our studies we have used most recent values of Van Zyl et al. (1983), measured with the TIF technique. An accurate procedure for obtaining absolute values for cross sections used by them involves calibration based on several independent measurements of emission cross sections in collisions of 500 eV- e^- with He, Ar, Kr, and N_2 .

Frequently, in the determinations of N_2^+ abundance (for instance for N_2^+/CO^+ ratio in comets, Cochran 2002), the (0, 0) band of $N_2^+(B-X)$ at 391.4 nm is used. From computer simulations it shows that the $N_2^+(B-X)$ abundance determined only from emission of 391.4 nm band could be distorted by excitation conditions leading to variations in vibrational temperatures. The $\Delta v = 0$ band at 391.4 nm makes 70% of all spectra for low temperature (1000 K) and decreases by a factor of 3.5 down to 20% for high temperatures (15 000 K).

Furthermore, if the excitation occurs in the collisions of hydrogen ions with the N_2 molecule (comets, molecular clouds interacting with stellar wind), for determining the abundance of the N_2 molecule from emission spectra, it is also important to also take the presence of N_2 emission into account, along with the emission from charge transfer N_2^+ products. We found that, in the 10–1000 eV energy range, the N_2^+/N_2 ratios for H^+ , H_2^+ , and $H_3^+ + N_2$ are in the range of (0.4–3.8), (0.9–1.2), and (0.6–1.5), respectively. Once again, in the case of H_2^+ and H_3^+ ions, these ratios are similar, and the N_2/N_2^+ fraction is almost 1:1, while for $H^+ + N_2$ at higher energies, N_2^+ dominates.

5. Conclusions

Spectroscopic studies of collisions between H^+ , H_2^+ , H_3^+ ions and nitrogen molecule under controlled conditions in the laboratory give unique opportunity for testing the interaction of ion flux (for instance stellar wind) with interstellar molecular clouds. In our studies we can give the possible processes taking place in the investigated collision systems:



where $n = 1, 2, 3$ and $[H]_n^+$ stand for the unknown state of the remaining products in the process.

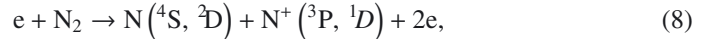
The charge transfer process of the type (4) and direct impact ionization (5) of the target molecule will result in the formation of N_2^+ either in ground or excited states. Unfortunately, both processes cannot be distinguished in our experiment. However, in the energy range presented in this paper the ionization process (5) is of minor importance. If we compare the total cross section for ionization (process 5) measured by De Heer & Aarts (1970) and for charge transfer (process 4) obtained by Hoffman et al. (1981) for the $H^+ + N_2$ system at 10 keV, we notice that about 5% of events will lead to ionization, while about 80% will result in ionization at 100 keV energy. Because the ionization

cross section decreases for low energies, while the charge transfer cross section increases, thus for a lower projectile energies the charge transfer process will dominate.

Process of type (6) is the direct impact excitation of target molecule leading to N_2 excitation.

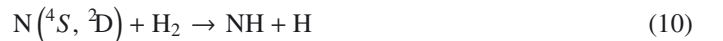
The fourth possible process is the formation of protonated nitrogen HN_2^+ , i.e. reaction path (7). The formation of HN_2^+ is efficient at low energies (<10 eV) and is unlikely at the higher energies used in present paper. Schultz & Armentrout (1992) measured the cross sections for formation of HN_2^+ in reactions of N_2^+ with H_2 , D_2 and HD at 0.1 up to 80 eV energies in the laboratory system. In the 0.1–80 eV energy range, the cross section for forming HN_2^+ decreases rapidly more than two orders of magnitude, reaching a value below 10^{-16} cm² for 80 eV energy and at still higher energies, it falls off even faster. Furthermore, at the lowest energies the charge transfer cross section is two orders of magnitude smaller than for HN_2^+ and shows little energy dependency. This means that at a given energy (above 20 eV in a center of mass) the charge transfer will dominate. Of course, this collision system differs from ours by changing the projectile ion with the target molecule, but Schultz & Armentrout (1992) have also shown that at very low energies the collision cross sections can be described well with the Langevin-Gioumousis-Stevenson model, where for reactions of $N_2^+ + D_2$ and $D_2^+ + N_2$, the cross section are the same order of magnitude and the same applies for the $N_2^+ + H_2$ and $H_2^+ + N_2$ cross section because the neutral polarizability of H_2 and D_2 is similar.

We have not found any evidence for electronically excited NH or NH^+ radicals, in the investigated spectral range, i.e. no trace of the $NH(A^3\Pi - X^3\Sigma)$ band at 336 nm or the $NH^+(B^2\Delta - X^2\Pi)$ band at 435 nm. The lack of the NH chemiluminescence signal can be explained by comparing it with other investigations of hydrogen-nitrogen collision systems. The electron impact dissociation of N_2 , according to the equation



will result in ionized and neutral nitrogen atoms in the ground or metastable electronic states.

The following reactions, including slow nitrogen and hydrogen atoms, leading to electronically excited NH and NH^+ were investigated:



Reaction (9) between N^+ in the ground 3P state and H_2 were reported in Kusunoki & Ottinger (1979). Reactions (10) for the ground $N(^4S)$ and metastable $N(^3D)$ states with H_2 , were presented in Ottinger et al. (1999) and Kowalski et al. (2004b), respectively. Kusunoki & Ottinger (1984) studied the excited NH^+ produced in the reaction (11) of the N^+ ion in the metastable 1D state. In these studies, the NH luminescence cross sections for reactions (9) and (10) exhibit the threshold behavior above approximately 4 eV, the peak maxima at energy between 8 and 15 eV due to an insertion-type reaction, and a rapid decrease in the cross section for higher energies, probably due to a two-body impulsive mechanism. In reaction (11), the maxima of NH^+ emission cross section is about 1.5 eV, decreasing thereafter monotonically with increasing energy (Kusunoki & Ottinger 1984). Thus, the NH or NH^+ signal is only observed in this narrow energy range.

This leads to the conclusion that the (10–1000 eV) H^+ and H_2^+ hydrogen ions present in the stellar wind, as well as H_3^+ encountering the N_2 molecule, cannot be the direct source of interstellar nitrogen monohydride NH. Instead, the N_2^+ ions produced in a charge transfer (reaction 4) or fragments arising from the electron impact dissociation (reaction 8) of N_2 impacting at the thermal energies of H_2 (reactions 9–11) or of other molecules could be the source of the observed NH or other polyatomic molecules (like HN_2^+ according with the reaction $N_2^+ + H_2 \rightarrow HN_2^+ + H$, Adams & Smith 1981).

It has been shown that electron excitation can be satisfactorily described by a model of vertical ionization (Franck-Condon principle) for $N_2(X^1\Sigma_g^+, v = 0)$ to N_2^+ at electron energies greater than 100 eV. For H_2^+ and H_3^+ collision systems, the enormous increase in the vibrational temperature (see Fig. 4) indicates that at certain energies the transition is of non-Franck-Condon type. Beyond this range the reaction is well described by vertical transition model.

While the projectile ion approaches the target molecule, the electron cloud of the target molecule will be deformed by ion field before the moment when one electron from molecule is captured. This probably will result in a change in the internuclear distance of the molecule and perturbation of the vibrational wave functions. For very slow projectile velocities, the ion will not approach the molecule close enough before electron capture, so the deformation will be negligible. At very high velocities, the ion will immediately reach the distance where electron capture is inevitable, while the internuclear distance will not manage to change significantly in a very short period of time. Thus, at very low and very high velocities the distortion of vibrational populations (thus the increase in vibrational temperature) is minor.

Forsén & Roos (1970) investigated the consequence of adding a proton to the closed-shell N_2 molecule and found that this will have a negligible effect on N_2 internuclear distance (about 0.1%) leading to the weak vibrational excitation of the nitrogen molecule. This would explain why the $H^+ + N_2$ has a vibrational temperature lower than for two other ions. The H_2^+ and H_3^+ ions probably have a stronger influence on the electron cloud, causing the change in internuclear distance between N_2 nuclei.

The dependency of vibrational temperatures on projectile velocity could be used to infer the energies of projectiles producing the emission of N_2^+ , for example, in comets or aurora. Another conclusion is that in the collision systems investigated, the excitation conditions affect the N_2^{+*} emission spectra as observed, for instance, in the comets or molecular clouds, thus could be the source of uncertainties in spectroscopically determined ratios of molecular nitrogen relative to various gases.

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