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Densities and Vibrational Distribution of H_3^+ in the Jovian Auroral IonosphereY. H. KIM¹ AND J. L. FOX

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Observations of the H_3^+ infrared emission at 2 and 4 μm have suggested that H_3^+ is in local thermodynamic equilibrium (LTE) in the region of the Jovian ionosphere from which the emissions originate. We have tested this assumption by calculating the vibrational distribution of H_3^+ over the altitude range of 350 to 1500 km above the methane cloud tops (1 to 4×10^{-3} μbar). We have constructed a model of the Jovian auroral ionosphere in which the neutral temperatures are enhanced over those of the mid-latitude ionosphere, as suggested by observations and models of the auroral region. We have modeled the precipitation of 10-keV electrons with an energy flux of $1 \text{ erg cm}^{-2} \text{ s}^{-1}$. Both the energy and energy flux are less than those that are implicated in the production of the UV aurora. We have computed the densities and vibrational distribution of H_3^+ and find that the distribution of the six lowest states of H_3^+ can be determined fairly well in spite of uncertainties in the atomic and molecular data. Since the nearly resonant transfer of vibration from $\text{H}_2(v=1)$ is an important process in populating the $\text{H}_3^+(v_1=0, v_2=2)$ state, it is necessary to model the vibrational distribution of H_2 as well. The computed altitude profiles and vibrational distributions of H_3^+ and H_2 are consistent with the observations of infrared emission in the 2- and 4- μm regions. The H_3^+ is not in LTE near and above the H_3^+ peak, since loss of the $\text{H}_3^+(v_1=0, v_2=1)$ and $\text{H}_3^+(v_1=0, v_2=2)$ states by radiation is approximately equal to the collisional loss rate.

INTRODUCTION

H_3^+ was detected spectroscopically for the first time in a celestial object in the Jovian southern auroral zone by Drossart *et al.* [1989]. They recorded high-resolution spectra of several infrared emission lines of the H_3^+ overtone transition, $2\nu_2(l=2) \rightarrow 0$ near 2 μm . Trafton *et al.* [1989] detected the lines but did not identify them. Drossart *et al.* derived a column density of $\text{H}_3^+(v_2=2, l=2)$ of $(1.39 \pm 0.13) \times 10^9 \text{ cm}^{-2}$ and a rotational temperature of $(1100 \pm 100) \text{ K}$ from the data. They suggested that although the emission appears to arise from altitudes above that of the UV aurora, electrons in the low-energy tail of the distribution could be responsible for production of H_3^+ above the ionospheric maximum. They also suggested that the $v_2=2$ vibrational levels could be produced either by resonant vibrational exchange with $\text{H}_2(v=1)$ or by collisional excitation. More recently, Oka and Geballe [1990] identified the 4- μm fundamental band of H_3^+ in the Jovian polar regions, and they estimated column densities of $\text{H}_3^+(v_2=1)$ ranging from 7 to 70 times the column density of $v_2=2$ reported by Drossart *et al.* [1989], and a lower rotational temperature of $(670 \pm 100) \text{ K}$. They failed to detect either the $v_2=2 \rightarrow 0$ overtone transition or the $v_2=2 \rightarrow 1$ hot band and concluded that the observed emissions did not arise from $\text{H}_3^+(v_2)$ produced directly in the reaction

but from the collisional excitation of $\text{H}_3^+(v_2=0)$ by H_2 or He. Miller *et al.* [1990] observed lines in the $\text{H}_3^+ \nu_2$ fundamental and overtone bands. From the ratios of the intensities, they derived a vibrational temperature of $(1100 \pm 100) \text{ K}$. They concluded that the agreement of this value with the rotational temperature measured by Drossart *et al.* [1989] implied that the vibrational distribution was in LTE.

H_3^+ has been known to be a major ion in the ionospheres of the outer planets, but the density profile has been uncertain because modelers have encountered difficulties reproducing the electron densities measured by the radio occultation experiments aboard the Voyager spacecraft [Waite *et al.*, 1983; Cravens, 1987; McConnell *et al.*, 1982; McConnell and Majeed, 1987]. Details can be found in the excellent review of measurements and models of the ionospheres of the outer planets by Atreya [1986]. The measured profiles showed electron densities about an order of magnitude smaller with a peak several hundred kilometers higher than those of models based on the chemistry of ground state species. In the models, H^+ was found to be the major ion over most of the ionosphere. McElroy [1973] had suggested that if sufficient quantities of $\text{H}_2(v \geq 4)$ were present, the H^+ densities could be reduced by the reaction

which is endothermic for H_2 in the first four vibrational levels. The resulting H_2^+ ions would be rapidly converted to H_3^+ and then lost by dissociative recombination. McConnell *et al.* [1982] pointed out that in addition to including (2), imposing vertical flow along field lines could raise the height of the peak. Waite *et al.* [1983] constructed a detailed model of the ionosphere of Jupiter and found that the electron den-

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sity profile could be brought into reasonable accord with the Voyager measurements if an H_2 vibrational temperature of 2500–4000 K, much higher than the neutral kinetic temperature, was assumed. Cravens [1987] modeled the H_2 vibrational distribution in the auroral and mid-latitude regions and showed that charge transfer from H^+ to vibrationally excited H_2 (reaction (2)) is an important chemical sink for H^+ in both the mid-latitude and auroral ionospheres. Moreover, the electron density profile for precipitation of 10-keV electrons with an energy flux of $10 \text{ erg cm}^{-2} \text{ s}^{-1}$ agreed fairly well with the Voyager 2 entry profile [Eshleman et al., 1979] when the H densities were reduced to 10% of the auroral values calculated by Waite et al. [1983].

Although the models of Waite et al. [1983] and Cravens [1987] included detailed ionospheric chemistry of H^+ , H_2^+ , and H_3^+ , individual density profiles of the ions were not presented. Cravens did state, however, that for the auroral cases, the H_3^+ density was almost as large as the H^+ density. McConnell and Majeed [1987] studied the effects of enhanced vibrational temperatures of H_2 on the density profiles of H_3^+ and H^+ in the Jovian ionosphere, and they investigated the effect of different assumptions about the dissociative recombination (DR) coefficient for H_3^+ . The value of this rate coefficient has been a matter of some controversy over the last several years. In 1984, Adams et al. [1984] measured the DR coefficient of H_3^+ in the vibrational ground state and found it to be “immeasurably small” ($< 2 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$) at 95 and 300 K, in contrast to previous measurements, which were in the range $(2\text{--}3) \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ [e.g., MacDonald et al., 1984]. Theoretical and experimental evidence suggested that higher vibrational levels recombined more rapidly [Michels and Hobbs, 1984], and the higher rates could be ascribed to the presence of vibrationally excited H_3^+ . McConnell and Majeed [1987] carried out a calculation in which two states of H_3^+ were considered: the ground vibrational state and a pseudostate that represented all vibrationally excited states, which they referred to as H_3^{+*} . They found that most of the vibrationally excited ions radiate to the ground state before recombining. They presented profiles of the ion densities for values of the DR coefficient for ground state H_3^+ that were 0.1, 0.01, and 0.001 times the standard values ($\sim 2 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$), which they assumed to be appropriate to vibrationally excited states. For values of the DR coefficient for ground state ions that were one thousandth of the excited state coefficient, H_3^+ was the dominant ion over most of the ionosphere. They also reported that both enhanced loss of H^+ by charge transfer to vibrationally excited H_2 and vertical ion flows were necessary to reproduce the measured ion peaks.

After the manuscript of McConnell and Majeed [1987] was prepared, Adams and Smith [1987] lowered their upper limit on the DR coefficient for ground state H_3^+ to $1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, a factor of 10^4 less than the standard values. Hus et al. [1988] measured the cross sections for DR of ground state H_3^+ in a merged beam and inferred a value for the rate coefficient of $2 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ at 100 K. Recently, however, Amano [1988, 1990], by measuring the decay of infrared absorption, reported a larger rate coefficient of $1.8 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ for recombination from the $J = 3, K = 3$ rotational state of the ground vibrational level. The controversy has not been clearly resolved, and the possibility that ground state and vibrationally excited H_3^+ recombine at radically different rates cannot yet be discounted.

Thus the vibrational distribution of H_3^+ is of interest for a number of reasons, including its emissions and possible effects on the chemistry. We have carried out a detailed calculation of the vibrational distribution of H_3^+ in the Jovian auroral ionosphere. We compare our computed distribution to the measured infrared emission rates. We then evaluate the effect of the distribution on the chemistry and structure of the ionosphere. In the rest of the discussion, altitude refers to height above the methane cloud tops, which is approximately the 0.6-bar level [cf. Atreya et al., 1981].

THE MODEL

Measurements and models have shown that temperatures in the auroral thermosphere are probably higher than those of the mid-latitude thermosphere. Drossart et al. [1989] reported a rotational temperature of $1099 \pm 100 \text{ K}$ for the first overtone transition of H_3^+ ; slightly smaller rotational temperatures of $670 \pm 100 \text{ K}$ were obtained by Oka and Geballe [1990]. If these temperatures apply to the region of the H_3^+ maximum, near 700 km (just below the 0.1- μbar level) [cf. McConnell and Majeed, 1987], then the auroral temperature is significantly higher than the mid-latitude value of 200–250 K at the 0.1- μbar level given by the Voyager stellar occultation data [Atreya et al., 1981]. Higher temperatures in the auroral zone were also predicted by Waite et al. [1983], who computed a significant heat input due to precipitating electrons. S. J. Kim et al. [1990] measured emission in the H_2 quadrupole lines in the auroral region, which also originate near 0.1 μbar ; the rotational temperature derived was 730 (+500, –200) K. The Voyager 2 entry radio occultation experiment indicated an ion temperature of 1600 K in the topside ionosphere [Eshleman et al., 1979]. We have constructed a model of the auroral thermosphere-ionosphere of Jupiter in which the temperatures and densities near the homopause are similar to the mid-latitude models, but the temperatures in the 1- μbar region and above increase to values that are consistent with the measured rotational temperatures. Our assumed temperature profile is shown in Figure 1 along with the density profiles of H_2 , He, and H atoms that were constructed self-consistently with the temperature profile. The density at a given altitude is larger than that inferred from the Voyager stellar occultation experiment in the nonauroral thermosphere [Atreya et al., 1981]. The atomic hydrogen densities are greatly affected by electron precipitation [Waite et al., 1983], and the H profile shown was obtained self-consistently in the calculation described below.

To account for (2) in our ionospheric model, we found that it was necessary to calculate the vibrational distribution of H_2 and the densities of the ions and H atoms together. The sources of vibrationally excited H_2 in the Jovian upper atmosphere have been discussed by Cravens [1987] and include direct excitation by electron impact, cascade from electronically excited states (mainly the $\text{B}^1\Sigma_u^+$ and $\text{C}^1\Pi_u$ states) due to electron impact excitation, solar UV fluorescence of H_2 , dissociative recombination of H_3^+ , and three-body recombination of H atoms. We essentially adopt the model of Cravens [1987] for all processes except solar UV fluorescence, which he did not include [cf. Majeed et al., 1990]. Vibrational excitation of H_2 due to solar UV fluorescence in the Lyman and Werner band system is calculated using the solar maximum flux of Hinteregger [see Torr et al., 1979] and the transition probabilities of Allison and Dal-

garno [1970]. The inclusion of fluorescence of solar UV radiation does not significantly affect H_2 vibrational distribution at low altitudes, but it becomes dominant at altitudes above 2500 km. Additional modifications to the model of Cravens [1987] include the adoption of the DR rate coefficient of $2 \times 10^{-8}(100/T)^{0.5} \text{ cm}^3 \text{ s}^{-1}$ for H_3^+ with a branching ratio of 1:3 between products, $H_2 + H$ and $H + H + H$ as measured by Mitchell et al. [1983], and the distribution of $H_2(v)$ in the three-body recombination of H atoms as calculated by Orel [1987].

We have included $H_2(v=0)$, $H_2(v=1)$, $H_2(v=2)$, and $H_2(v=3)$ separately, and we treat $H_2(v \geq 4)$ as a pseudostate that represents all vibrational states higher than $v=3$. The production rate of $H_2(v \geq 4)$ is thus simply the sum of production rates of individual states from the channels listed above plus collisional excitations from $H_2(v=3)$ to $H_2(v=4)$. The net loss of $H_2(v \geq 4)$ includes collisional and radiative de-excitation from $H_2(v=4)$ to $H_2(v=3)$. In addition, $H_2(v \geq 4)$ can be removed by the reaction with H^+ as assumed in previous Jovian ionospheric models [McConnell et al., 1982;

Waite et al., 1983; Cravens, 1987; McConnell and Majeed, 1987]. The rate coefficient, k_2 , has not been measured but is assumed to be $10^{-6} \text{ cm}^3 \text{ s}^{-1}$, which is close to the gas kinetic value. The collisional processes include vibration-vibration (VV) energy transfer reactions between $H_2(v)$ and $H_2(v')$, and vibration-translation (VT) energy transfer reaction $H_2(v)$ and H_2 and between $H_2(v)$ and H. The rate constants for these reactions are also adopted from expressions given by Cravens [1987]. The deexcitation of $H_2(v)$ via quadrupole radiative transitions is ignored since the transition probabilities are small, of the order of 10^{-6} s^{-1} . Diffusive equilibrium is assumed for the top boundary at 3700 km; photochemical equilibrium is assumed for the lower boundary at 200 km.

We have used a multistream electron transport code for the auroral electron precipitation. The code, which was developed by Porter et al. [1987], utilizes the full angular dependence of the differential elastic scattering cross section to track electron energy deposition. Twenty-one angular bins were used in our calculation along with 50 altitude bins and 200 energy bins. Both elastic and inelastic cross sections are needed for major constituents of Jovian thermosphere, H_2 , He, and H. The sources of these cross sections are listed in Table 1. We consider here the precipitation of 10-keV electrons with an energy flux of $1 \text{ erg cm}^{-2} \text{ s}^{-1}$. The energy flux is less than the flux estimated from the observed UV auroral emissions [Broadfoot et al., 1981; Sandel et al., 1979], and 10 keV is less than the energy required to produce the UV aurora [Livengood et al., 1990; Gladstone and Skinner, 1989; Yung et al., 1982]. Our goal here is to show that the H_3^+ and H_2 infrared emissions could be produced by the lower energy part of the precipitating electron distribution. The downward pitch angle distribution is assumed to be isotropic, and the electrons are injected at an altitude of 3700 km. Figure 2 shows the production rates of H_2^+ , H^+ (from H), and $H + H^+$ (from H_2) that are obtained from an iterative calculation in which the electron and H atom densities, which are produced mainly by electron precipitation, are computed self-consistently. In Figure 3 we present altitude profiles of the major sources of $H_2(v=1)$ and $H_2(v \geq 4)$,

Fig. 1. Density profiles of H_2 , He, and H and temperature profile in Jovian auroral upper atmosphere. The densities are calculated consistently with the adopted temperature profile and precipitation of 10-keV electrons with an energy flux of $1 \text{ erg cm}^{-2} \text{ s}^{-1}$.

TABLE 1. Electron Impact Cross Sections

Species	Processes	References
H_2	ionization	Rapp and Englander-Golden [1965]
	$B^1\Sigma_u^+$, $B'^1\Sigma_u^+$, $B''^1\Sigma_u^+$	Shemansky et al. [1985], Ajello et al. [1988]
	$C^1\Pi_u$, $D^1\Pi_u$, $D'^1\Pi_u$	Shemansky et al. [1985], Ajello et al. [1988]
	$E,F^1\Sigma_g^+$	Shemansky et al. [1985], Ajello et al. [1988]
	$c^3\Pi_u$, $a^3\Sigma_g^+$	Khakoo and Trajmar [1986]
	$b^3\Sigma_u^+$	Lima et al. [1985]
	$3p^3\Pi_u$	Möhlmann and De Heer [1976]
	$H(2p)$, $H(2s)$	Ajello et al. [1988], Mumma and Zipf [1971], Möhlmann et al. [1978]
	Balmer- α, β, γ	Möhlman et al. [1978], Freund et al. [1976]
	$v = 0 \rightarrow 1, 2, 3, 4, 5, 6$	Allan [1985], Ehrhardt et al. [1968]
He	ionization	Linder and Schmidt [1971], Fink et al. [1975], Shyn and Sharp [1981], Srivastava et al. [1975], van Wingerden et al. [1977]
	excitation	Jackman et al. [1977]
	elastic	Jackman et al. [1977]
H	ionization	Porter et al. [1987]
	excitation	De Heer et al. [1977, and references therein]
	elastic	Callaway and McDowell [1983]
		Williams [1975a, b]

Fig. 2. Computed production rate profiles for H_2^+ , $H + H^+$ (from H_2) and H^+ (from H) due to the precipitation of 10-keV electrons with an energy flux of $1 \text{ erg cm}^{-2} \text{ s}^{-1}$ into the auroral upper atmosphere model shown in Figure 1.

Fig. 3. Computed production rate profiles for $H_2(v=1)$ and $H_2(v=4)$ by direct excitations (solid curves) and by cascading from $B^1\Sigma_u^+$ and $C^1\Pi_u$ states (dashed curves) due to the electron precipitation described in Figure 2.

Fig. 4. Density profiles of ions and $H_2(v)$ due to the precipitation of 10-keV electrons with an energy flux of $1 \text{ erg cm}^{-2} \text{ s}^{-1}$ into the auroral upper atmosphere.

which include direct excitation from $H_2(v=0)$ and cascading from the $B^1\Sigma_u^+$ and $C^1\Pi_u$ states.

The calculated density profiles of H^+ , H_3^+ , $H_2(v=1)$, and $H_2(v=4)$ are shown in Figure 4. The lower peak in the

$H_2(v=4)$ profile at 350 km in Figure 4 is due to the three-body recombination of H atoms that produces $H_2(v=4)$. The increase of the $H_2(v=4)$ densities above 580 km is caused by a combination of excitation by precipitating electrons and VV transfer from H_2 . For example, at 850 km the production rate of $H_2(v=4)$ from the electron precipitation is $129 \text{ cm}^{-3} \text{ s}^{-1}$, while the rate of collisional excitation of $H_2(v=3)$ by $H_2(v=1)$ (VV transfer) is $626 \text{ cm}^{-3} \text{ s}^{-1}$. The collisional deexcitation of $H_2(v=4)$ to $H_2(v=3)$ due to the VV reaction is the major loss channel, resulting in a lifetime of 2.4 s for $H_2(v=4)$. The estimated density of $H_2(v=4)$ is then about $1.8 \times 10^3 \text{ cm}^{-3}$. In general, the collisional excitation and deexcitation due to the VV reactions are more important than the other sources and sinks of $H_2(v=4)$ in this altitude region. The production of $H_2(v=4)$ by electron precipitation decreases with altitude (see Figure 3), whereas the production due to collisional excitation continues to increase as the temperature rises up to 1500 km ($\sim 4 \times 10^{-3} \mu\text{bar}$), where we have arbitrarily assumed the exospheric temperature of 1600 K is reached. Even if the actual temperature profile differs from our assumed profile above 0.1 μbar , the results will not change qualitatively.

We find that the ratio of $H_2(v=1)$ to $H_2(v=0)$ is close to the LTE value at all altitudes because the rate of production of $H_2(v=1)$ by electron precipitation is much smaller than the rate of VT reactions with H_2 and H . For example, at 750 km the peak production rate of $H_2(v=1)$ from the precipitation is $1.2 \times 10^3 \text{ cm}^{-3} \text{ s}^{-1}$, which is much smaller than $3.4 \times 10^7 \text{ cm}^{-3} \text{ s}^{-1}$, the production rate due to VT reactions with H atoms. Thus the $H_2(v=1)$ density profile fully reflects the adopted temperature profile, which results in a broad peak around 700 km (near 0.1 μbar) where the assumed temperature is 950 K. The column density of $H_2(v=1)$ is $1.8 \times 10^{17} \text{ cm}^{-2}$. The density profile of $H_2(v=1)$ is therefore consistent with the observations of H_2 quadrupole line emissions, which imply a column density of $(1-4) \times 10^{17} \text{ cm}^{-2}$ for $H_2(v=1)$ [S. J. Kim et al., 1990].

The H_3^+ density is inversely proportional to the electron density, that is, the H^+ density at most altitudes, and proportional to the production rate of H_2^+ . Therefore the density peak of H_3^+ occurs at the lower edge of the H^+ density profile at 650 km. The lower shoulder of H_3^+ at about 450 km in Figure 4 is caused by impact ionization of H_2 by photoelectrons released in photoionization by solar soft X rays. The profile of H_3^+ also forms a broad upper shoulder between 800 and 1500 km where the H_3^+ production by (1) and loss by DR vary with altitude at nearly the same rate. The density profile of H_3^+ at altitudes higher than 1500 km follows the $H_2(v=4)$ profile because the reaction between $H_2(v=4)$ and H^+ is the main source of H_3^+ , which in turn produces H_3^+ . The column density of H_3^+ is $2.6 \times 10^{12} \text{ cm}^{-2}$, which is within the range of $(0.1-1) \times 10^{13} \text{ cm}^{-2}$ estimated from the IR observations of Drossart et al. [1989]. The peak density and column density of H_3^+ are inversely proportional to the adopted DR rate constant but are rather weakly affected by the assumed energy flux of the precipitating electrons. An increase in the energy flux enhances both the production of H_3^+ and loss by DR as the electron density increases. The densities of H^+ and H atoms, however, increase with the energy flux of the precipitating electrons. We show in Table 2 the results of alternative models in which the computed column densities of H_3^+ and H^+ are given for combinations of the energy flux of 0.1, 1, and $10 \text{ erg cm}^{-2} \text{ s}^{-1}$ and the DR

TABLE 2. Computed Column Densities of H_3^+ and H^+

$\alpha(\text{H}_3^+)$ at $T = 100 \text{ K}$ ($\text{cm}^3 \text{ s}^{-1}$)		Energy Flux of 10-keV Electrons, ($\text{erg cm}^{-2} \text{ s}^{-1}$)		
		0.1	1	10
2×10^{-8}	H_3^+	2.7×10^{12}	2.6×10^{12}	2.5×10^{12}
	H^+	1.0×10^{13}	1.4×10^{14}	1.2×10^{15}
2×10^{-9}	H_3^+	1.7×10^{13}	1.8×10^{13}	2.2×10^{13}
	H^+	1.5×10^{13}	1.4×10^{14}	1.2×10^{15}

The unit of column density is cm^{-2} .

rate coefficients, $\alpha(\text{H}_3^+)$, of 2×10^{-8} and $2 \times 10^{-9}(100/T)^{0.5} \text{ cm}^3 \text{ s}^{-1}$.

The densities of H^+ in Figure 4 are somewhat larger than the observed electron densities of the Voyager 2 entry radio occultation experiments, as they have been in other models also. The densities of H^+ tend to increase with the densities of H, which were enhanced in Figure 4 by electron precipitation. Since the enhanced H densities in auroral regions may be reduced due to thermospheric winds as suggested by Waite *et al.* [1983], the H^+ densities in Figure 4 must be considered as upper limits. In addition, there is a significant uncertainty in the DR rate coefficient of H_3^+ as discussed earlier. One can generate the H^+ densities close to the observed electrons densities between 900 and 1500 km without altering the H_3^+ densities in Figure 4 by reducing the H densities and adopting a larger value of $\alpha(\text{H}_3^+)$. Since our main purpose here is to explain the vibrational distribution of H_3^+ , we have chosen not to carry out these somewhat ad hoc adjustments.

The high temperatures in our models result in an extended thermosphere so that for the sunlit auroral regions the solar UV photons ionize H_2 and H at high altitudes: the ionization peaks of H_2 and H are at 1800 km and 3000 km, respectively. These ionizations are sources of H^+ at high altitudes ($> 1800 \text{ km}$) where the $\text{H}_2(v \geq 4)$ density is not large enough to reduce H^+ . Consequently, the H^+ density profile does not decrease at altitudes above 1500 km as does the observed electron density profile of the Voyager 2 entry radio occultation experiments. Significant reduction of H^+ could occur at high altitudes due to additional production of $\text{H}_2(v \geq 4)$ by soft electrons. Alternatively, as Waite *et al.* [1983] suggested, thermospheric winds could reduce the H densities significantly, thus reducing the loss of $\text{H}_2(v \geq 4)$ by H atom quenching and increasing the rate of (2). If the H^+ densities are reduced to the observed values at high altitudes via the additional processes, the H_3^+ densities would increase by a factor of 10 at these altitudes, but the bulk of the H_3^+ column density would still remain below 1500 km. In the discussion that follows therefore we consider only the vibrational distribution of H_3^+ below 1500 km.

H_3^+ VIBRATIONAL DISTRIBUTION

The observed H_3^+ infrared emission is due to radiative relaxation of vibrationally excited H_3^+ . H_3^+ has two vibrational modes, a symmetric breathing mode ν_1 , with quantum number v_1 , and a doubly degenerate asymmetric bending mode ν_2 , with quantum number v_2 . The first-order energy separation of the symmetric and asymmetric modes are 0.39 and 0.31 eV, respectively. Reaction (1) is exothermic by 1.7

eV, and the H_3^+ produced is vibrationally excited, although the exact distribution is unknown [J. K. Kim *et al.*, 1974; Smith and Futrell, 1975]. Anicich and Futrell [1983/1984] computed the nascent distribution assuming that the excess energy is partitioned between translation and vibrational modes in a statistical manner. We carried out a slightly more elaborate calculation in which we included the rotational degrees of freedom as well as translation and vibration, as discussed, for example, by Levine and Bernstein [1974] [cf. Fox, 1988]. We have included 55 states labeled by (v_1, v_2) with $v_1 + v_2 \leq 9$, whose energies were computed from the term values given by Majewski *et al.* [1987]. The average vibrational energy of the nascent H_3^+ in our calculation, 0.90 eV, is less than that of Anicich and Futrell [1983/1984], 1.32 eV, because with the addition of rotational degrees of freedom, the lower vibrational levels become more probable. The use of our distribution over that of Anicich and Futrell does not, however, substantially affect the results.

Vibrational levels are interchanged by radiation and collisional excitation and deexcitation. For radiative relaxation of levels whose energies are less than 0.9 eV, namely $(0,1) \rightarrow (0,0)$, $(0,2) \rightarrow (0,0)$, $(1,1) \rightarrow (0,0)$, $(0,3) \rightarrow (0,0)$, $(1,0) \rightarrow (0,1)$, $(0,2) \rightarrow (0,1)$, $(1,1) \rightarrow (0,1)$, $(2,0) \rightarrow (0,1)$, $(0,3) \rightarrow (0,1)$, $(0,2) \rightarrow (1,0)$, $(1,1) \rightarrow (1,0)$, $(0,3) \rightarrow (1,0)$, $(1,1) \rightarrow (0,2)$, $(0,3) \rightarrow (0,2)$, $(2,0) \rightarrow (1,1)$, and $(0,3) \rightarrow (1,1)$ we have adopted the Einstein A coefficients (transition probabilities) computed by S. Miller (private communication, 1991) [cf. Miller and Tenyson, 1989]. The Einstein A coefficients are of the order of 100 s^{-1} for transitions in which only v_2 changes by one quantum and of the order of 1 s^{-1} for transitions in which both v_1 and v_2 change. Transitions in which only v_1 changes are dipole forbidden. For radiative relaxation of levels with energy greater than 0.9 eV, we assume an average Einstein A coefficient of 100 s^{-1} for transitions of the type $(v_1, v_2) \rightarrow (v_1, v_2 - 1)$, and we ignore transitions in which both quantum numbers change.

Excitation and deexcitation can occur owing to collisions with the surrounding gas, mainly H_2 and H. Quenching by H_2 can occur either by vibrational transfer without atom transfer or by chemical reaction such as proton transfer. There are no direct measurements of rate coefficients of the elementary processes occurring during quenching by H_2 , but J. K. Kim *et al.* [1974] measured a "phenomenological" rate coefficient of $2.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for the deactivation of H_3^+ with vibrational energies of 0.5–2.5 eV by H_2 . Little dependence of deactivation rate was observed with vibrational energy of H_3^+ , although there was some evidence that the effective rate coefficient increased slightly with vibrational energy level. The phenomenological rate coefficient is close to the rate coefficient $3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for the proton transfer reaction $\text{H}_3^+ + \text{D}_2 \rightarrow \text{HD}_2^+ + \text{H}_2$, measured by Terao and Back [1969]. We treat the quenching reaction of H_3^+ by H_2

alternatively as a proton transfer reaction in which complete deactivation (to the H_3^+ vibrational ground state) occurs or as a VV transfer process in which the H_2 gains 1–3 quanta of vibrational energy. We then test the sensitivity of the model to these assumptions. In the former case, we adopt the phenomenological rate coefficient of J. K. Kim *et al.* [1974]. In the latter case, we assume the transfer of vibrational energy from H_3^+ producing $\text{H}_2(v)$, where $v = 1, 2$, or 3, are equally

TABLE 3. Assumed Reaction Rate Coefficients of Vibration-Vibration Transfer from H_3^+ to H_2

Vibrational Energy of H_3^+	Number of Quanta Gained by H_2		
	1	2	3
$0.5 \leq E_{vib} < 1.0$ eV	2.7×10^{-10}		
$1.0 \leq E_{vib} < 1.5$ eV	4.3×10^{-10}	4.3×10^{-10}	
$1.5 \leq E_{vib}$	6.3×10^{-10}	6.3×10^{-10}	6.3×10^{-10}

Rate coefficients are in unit of $\text{cm}^3 \text{s}^{-1}$.

probable, and we adopt the rate coefficients shown in Table 3, which results in quenching rates approximately equal to those measured by *J. K. Kim et al.* [1974]. VV transfer cannot occur for states of H_3^+ for which the vibrational energy is less than the energy spacing of H_2 , about 0.5 eV. *Blakley et al.* [1977] experimentally estimated a VT quenching rate coefficient

of the order of $10^{-12} \text{ cm}^3 \text{s}^{-1}$ for low vibrational levels, and we adopt this value.

H_3^+ can also be deexcited by collisions with H atoms:

The rate coefficient for this reaction is unknown, but quenching by reactive species such as H atoms has been observed to be efficient, especially where the reaction can take place by atom transfer. We therefore assume a gas kinetic rate coefficient of $3 \times 10^{-9} \text{ cm}^3 \text{s}^{-1}$ for (5), and we arbitrarily assume that the H_3^+ is quenched to the vibrational energy level immediately below the initial level.

Collisional excitation of H_3^+ by H_2 and H, the reverse of (3), (4), and (5), is also included with rate coefficients determined by detailed balance. We ignore quenching of H_3^+ by electrons because the rate constant of about $5 \times 10^{-9} \text{ cm}^3 \text{s}^{-1}$, estimated from a general formula by *Neufeld and Dalgarno* [1989], is not large enough for this process to be significant.

RESULTS AND DISCUSSION

We have computed the vibrational distribution of H_3^+ assuming photochemical equilibrium. That this is a valid assumption over most of the H_3^+ layer can be seen by comparing the chemical lifetime of vibrational states at the 10^{-3} - μbar level (2000 km), which is about 10 s, to the diffusion lifetime, about 10^5 s. In our standard model, we adopt the VV rate coefficients for (3) from Table 3.

The loss and production profiles of the (0,1) state are presented in Figure 5, where short dashed and solid curves represent the VT transfer reactions with H_2 and H (reactions (4) and (5)), respectively. Figure 5a shows the loss rates of the (0,1) state by collisional deexcitation to the (0,0) state, collisional excitation to the (1,0) state, and radiative decay to the (0,0) state. Figure 5b shows the production rates of the (0,1) state by the reverse collisional processes presented in Figure 5a. The rate of collisional production from the (0,0) state is much greater than the collisional loss to the (0,0) state at altitudes above the H_3^+ peak. The presence of radiative decay therefore causes the densities of the (0,1) state to be much less than those of a thermal distribution

Fig. 5. (a) Loss rate and (b) production rate profiles of the $\text{H}_3^+(0,1)$ state via vibration-translation (VT) reaction with H (solid curve), VT reaction with H_2 (short dashed curve), and radiative decay (long-dashed curve). The initial (for production) or final (for loss) states of these reactions are presented near the curves.

at high altitudes. Figure 5 also shows that the VT reaction with H controls the densities of the $\text{H}_3^+(0,1)$ and $\text{H}_3^+(1,0)$ states whose energies are less than the vibrational energy spacing of H_2 . At 650 km the excitation rate from (0,0) to (0,1) by the reverse of (5) is $4 \times 10^5 \text{ cm}^3 \text{s}^{-1}$, whereas the production rate from any other channels is smaller by an order of magnitude. The specific loss rate for the (0,1) state by (5) is 150 s^{-1} at 650 km, which is comparable to the Einstein A coefficient of 120 s^{-1} . From these values one can estimate roughly a density of $2 \times 10^3 \text{ cm}^{-3}$ for the (0,1) state. The VT reaction with H_2 can also excite and deexcite the (0,1) state but is slower by 2 orders of magnitude than the VT reaction with H atoms.

A similar analysis can be carried out for the (0,2) state. The loss and production rate profiles are shown in Figures 6a and 6b, respectively. The VT reactions are shown as in Figure 5, along with excitation and deexcitation rates via the VV transfer reaction with H_2 . Radiative decay is the dominant loss channel of the (0,2) state at altitudes near and above the H_3^+ peak, and the dominant production rate is the VV reaction with $\text{H}_2(v=1)$. The rate constant for the excitation reaction from (0,0) to (0,2) is 57% of the deexcitation rate constant at 900 K due to the near resonance of vibrational energy levels between $\text{H}_2(v=1)$ and $\text{H}_3^+(0,2)$. At 650 km, for example, the excitation rate from (0,0) to (0,2) is $4 \times 10^4 \text{ cm}^{-3} \text{ s}^{-1}$, the density of $\text{H}_2(v=1)$ is $2.5 \times 10^9 \text{ cm}^{-3}$, and the temperature is 900 K. The specific deexcitation rate from (0,2) to (0,0) due to the VV reaction is 500 s^{-1} at this altitude, which is comparable to the Einstein A coefficient of 360 s^{-1} for the (0,2) state. A rough estimate from these values gives a density of 40 cm^{-3} for the (0,2) state.

Computed altitude profiles of the densities of the six lowest states (v_1, v_2) are shown in Figure 7. We find that the distribution of the lowest states other than the (2,0) state is almost independent of the choice of the average Einstein A coefficient used for the higher states and is also insensitive to assumptions about the quenching of high vibrational states

Fig. 6. (a) Loss rate and (b) production rate profiles of the $\text{H}_3^+(0,2)$ state via vibration-translation (VT) reaction with H (solid curve), VT reaction with H_2 (short dashed curve), vibration-vibration reaction with H_2 (dot-dashed curve), and radiative decay (long-dashed curve). The initial or final states of these reactions are presented near the curves.

Fig. 7. Computed density profiles for the six lowest vibrational states of H_3^+ due to the precipitation of 10-keV electrons with an energy flux of $1 \text{ erg cm}^{-2} \text{ s}^{-1}$ into the auroral upper atmosphere. For comparison, the dashed curves show densities of the (1,0) and (0,2) states from a model that excludes the vibration-vibration reaction with $\text{H}_2(v=1)$.

Fig. 8. Vibrational distributions of H_3^+ . The computed vibrational distribution at 650 km is shown by solid polygons. A Boltzmann distribution of 900 K and the nascent distribution used in the model are also presented with open polygons and stars, respectively.

by H_2 . The density of the (2,0) state is slightly affected by these assumptions, since it is produced partially by collisional deexcitation from the higher states. Different assumptions about the nascent distribution of $\text{H}_3^+(v_1, v_2)$ have also virtually no effect on the resulting distribution of the lower states. The calculated column densities of (0,2) and (0,1) are 2.3×10^9 and $6.1 \times 10^{10} \text{ cm}^{-2}$, respectively, and are consistent with observations of H_3^+ IR emissions, which indicate column densities of (0,2) and (0,1) of the order of 10^9 and 10^{10} cm^{-2} , respectively [Drossart et al., 1989; Oka and Geballe, 1990; Miller et al., 1990]. The average temperature over the (0,2) column is also consistent with the observed rotational temperature of $1099 \pm 100 \text{ K}$ by Drossart et al. [1989] and the rovibrational temperature of $1100 \pm 100 \text{ K}$ by Miller et al. [1990] for our assumed temperature profile.

The fractions of vibrational levels as a function of energy at the H_3^+ peak ($\sim 0.2 \mu\text{bar}$) are shown in Figure 8, in which the solid polygons represent the model results, and the open polygons a Boltzmann distribution at the local temperature (LTE). The nascent distribution assumed is indicated by the stars. In the model distribution, the fractions of the

lowest vibrational levels (with energies less than 1.4 eV) are smaller than but close to those of a Boltzmann distribution. Our computed distribution of states with energies greater than 0.9 eV should be considered as qualitative, since the Einstein A coefficients and rate constants may differ significantly from the assumed values for the high-energy states. The total fraction of these states is, however, of the order of 10^{-4} , and their distribution therefore does not affect that of the five lowest states presented in Figure 7.

To demonstrate the role of $\text{H}_2(v=1)$, we have constructed a model that excludes the VV reaction with $\text{H}_2(v=1)$. The resulting densities of the (1,0) and (0,2) states of H_3^+ are shown with the dashed curves in Figure 7. The densities of (0,2) are reduced by about an order of magnitude from the densities in the standard model. The observed H_3^+ IR emissions are thus related to the observed H_2 quadrupole emissions. The $\text{H}_2(v=1)$ density of a few times 10^9 cm^{-3} required for the VV transfer to H_3^+ is consistent with a column density of $\text{H}_2(v=1)$ of a few times of 10^{17} cm^{-2} estimated from H_2 IR quadrupole line observations [S. J. Kim *et al.*, 1990]. The precipitating electrons that are responsible for the observed H_3^+ IR emissions should deposit most of their energy in an altitude region where a sufficient density of $\text{H}_2(v=1)$ is available for the VV transfer to H_3^+ . Since the $\text{H}_2(v=1)$ density cannot be larger than the total H_2 density, the peak of the H_3^+ emission must be below the 10^{-3} - μbar level. The emission must also be above the methane homopause because at those altitudes hydrocarbon molecules destroy H_3^+ quickly by charge transfer reactions [cf. Kim and Fox, 1991]. The 10-keV electrons deposit most of their energy between these limits, namely, at around 0.1 μbar .

CONCLUSIONS

We have shown that precipitation of 10-keV electrons with a flux of about $1 \text{ erg cm}^{-2} \text{ s}^{-1}$ produces vibrational distributions of H_2 and H_3^+ that are consistent with the IR line observations in Jovian auroral regions. We have examined the collisional relaxation processes of H_3^+ vibrational states, and we find that distribution of the six lowest vibrational states of H_3^+ can be determined fairly well in spite of uncertainties about H_3^+ vibrational relaxation. We find that the VV transfer reaction between the near-resonant $\text{H}_2(v=1)$ and $\text{H}_3^+(v_1=0, v_2=2)$ states is important in determining the population of the $\text{H}_3^+(v_1=0, v_2=2)$ state. In our model, the $\text{H}_2(v=1)$ and H_3^+ densities peak at about the same altitude, around 650 km ($\sim 0.2 \mu\text{bar}$). At the peak of the H_3^+ profile, radiative decay of the (0,1) and (0,2) states is nearly as important as collisional deexcitation. Therefore the vibrational distribution at the peak is not a thermal distribution, as suggested by Miller *et al.* [1990] and Drossart *et al.* [1989], but the fractional populations of the (0,1) and (0,2) states at the H_3^+ peak are only slightly smaller than those of a Boltzmann distribution.

At the time of submission of this manuscript, images of $\text{H}_3^+ \nu_2$ fundamental band emission at 3–4 μm in the Jovian polar regions have been presented [S. J. Kim *et al.*, 1991; Baron *et al.*, 1991]. These observations indicate that the maximum H_3^+ emission does not coincide with the UV and IR hot spot, at least in the northern polar region. The precipitating electrons in our model are characterized by both lower energies and lower energy fluxes than those inferred from the UV aurorae. Our model is therefore not inconsistent with these observations.

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