VIBRATIONAL DISTRIBUTION FUNCTIONS AND EFFECTIVE VIBRATIONAL TEMPERATURE IN N₂-H₂ MIXTURE FLOW DISCHARGE

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Abstract

The effective vibrational temperature of \( \text{N}_2 \chi^1 \Sigma_g^+(v) \) molecules and some electrophysical parameters of plasma are measured in the positive column of a d.c. discharge in \( \text{N}_2\text{-H}_2 \) mixture. Based on self-consistent solution of Boltzmann equation and a system of rate balance equations for \( \text{N}_2(X) \) and \( \text{H}_2(X) \) vibrational levels the vibrational distribution functions for \( \text{N}_2(X) \) and \( \text{H}_2(X) \) molecules and other data are calculated. A good agreement between experimental results and calculation data has been found. It has appeared that the values of vibrational temperature of \( \text{N}_2(X, v) \) molecules are increased from 4500 K to 8300 K while the \( \text{N}_2 \) percentage is decreased from 100% to 10%.

1. Introduction

It is well known that the low-pressure plasma represents highly nonequilibrium system, where temperature of separate components can strongly differ. Such feature of this plasma defines its high chemical activity. Low-pressure discharges in \( \text{N}_2 \) and \( \text{N}_2\text{-H}_2 \) mixtures are widely used as a source of active species for plasma chemical treatment of materials, polymer modification and chemical synthesis of various molecules. The vibrationally excited molecules (VEM) are one of such active species. The subject of the present work is devoted to experimental determination of effective vibrational temperature of \( \text{N}_2 \chi^1 \Sigma_g^+(v) \) molecules in \( \text{N}_2\text{-H}_2 \) mixture plasma and to estimation of vibrational distribution functions (VDF) by numerical methods.

2. Experimental details

The discharge is produced in a glass (molybdenum sealing) cylindrical reactor with 15-mm inner diameter at gas pressure \( p = 266 \text{ Pa} \), flow rate \( Q \approx 2.0 \text{ cm}^3/\text{s (STP)} \) and discharge current up to 100 mA [1,2]. An initial composition of \( \text{H}_2\text{-N}_2 \) mixture was set by the changing of the gas flow velocity balance under the fixed pressure. Such parameters as electric field strength, gas and wall temperatures were measured.

The determination of effective vibrational temperature of \( \text{N}_2 \chi^1 \Sigma_g^+(v) \) molecules was carried out by a radiation spectroscopy via registration of the 2nd positive system bands of nitrogen (\( C^2 \Pi_u \rightarrow B^2 \Pi_g \)) and by subsequent mathematical treatment with use of numerical
techniques. We considered the populations of the first five levels of \( N_2(C^1\pi_u) \), which could be determined experimentally.

For the experimental conditions mentioned before, the electron density is of the order \( 10^{10} \text{ cm}^{-3} \) and the state \( N_2(C^1\pi_u) \) can be considered to be populated by direct electron collision from the state \( N_2(X^1\Sigma_g^+) \) and de-populated by radiative transition to the state, with emission of the second positive system. It was noted that in this case the vibrational distribution of \( N_2(C^1\pi_u) \) approaches the distribution obtained by electron-impact excitation which occurs according to the Frank–Condon principle and the vibrational levels are populated proportionally with the Frank–Condon factors \( q_{\chi C}(v,v') \) of the transition \( X^1\Sigma_g^+ \rightarrow C^1\pi_u, v' \). So the concentrations of the vibrational levels are related to the ground state vibrational distribution by \[ N_2(C,v') = \sum_v q_{\chi C}(v,v') N_2(X,v) \] Thus, knowing the vibrational distribution of \( N_2(C^1\pi_u) \) we solved the Boltzmann equation for electrons so that to find the vibrational distribution of \( N_2(X^1\Sigma_g^+) \) satisfying to experimental data.

3. Numeric calculation details

To calculate vibrational distribution functions the modelling of the processes for \( N_2(X) \) and \( H_2(X) \) vibrational kinetics has been accomplished. The modelling was based on solving Boltzmann equation, which were coupled to a system of rate balance equations for \( N_2(X) \) and \( H_2(X) \) vibrational levels. The Boltzmann equation took into account the elastics, inelastic, and superelastic collisions of electrons with \( N_2(X,v) \), \( H_2(X,v') \), \( H(\cdot \Sigma) \), and \( N(\cdot \Sigma) \). Vibrational kinetic equations included \( V-V, V-T \) single-quantum energy exchange between the same and different \( N_2, H_2 \), \( N, H \) partners as well as \( e-V, h-V \) processes and some others. A number of processes are listed in tables 1 and 2.

| Table 1. Inelastic and superelastic processes in the electron Boltzmann equation \[1,2\] |
|---|---|
| **Nitrogen** | e + \( N_2(X,v) \) ⇔ e + \( N_2(X,w) \), \( v = 0, ..., 8 \); \( w = v + 1, ..., 9 \)  
 e + \( N_2(X,v = 0) \) → e + \( N_2(Y) \), \( Y = a^1\Sigma_u^+, B^1\Pi_g, W^3\Delta_u, B^3\Sigma_u^- 
 a^1\Sigma_u^+, a^1\Pi_g, w^3\Delta_g, C^1\Pi_u, E^3\Sigma_g^+, a^1\Sigma_u^+, c^1\Sigma_u^+, c^1\Pi_u, b^1\Pi_u, b^1\Sigma_u^+ 
 e + \( N_2(X,v = 0) \) → e + \( N_2^2 \) + e  
 e + \( N(\cdot \Sigma) \) → e + \( N(\cdot \Sigma, \cdot \Pi) \)  
 e + \( N(\cdot \Sigma) \) → e + N^+ + e |
| **Hydrogen** | e + \( H_2(X,v') \) ⇔ e + \( H_2(X,w') \), \( v' = 0, ..., 3 \); \( w' = v' + 1, ..., 4 \)  
 e + \( H_2(X,v') \) → e + \( H_2(Y) \), \( Y = B^3\Sigma_u^+, E^3\Pi_u, a^3\Sigma_g^+, c^3\Sigma_u^+, B^1\Pi_u, E^1\Sigma_g^+, F^1\Pi_g, B^3\Sigma_u^+, B^1\Pi_u, B^3\Pi_u, D^1\Pi_u, D^3\Pi_u 
 e + \( H_2(X,v' = 0) \) → e + \( H(\cdot \Sigma) + H(\cdot \Pi) \) \( n = 2, 3 \)  
 e + \( H_2(X,v' = 0) \) → e + \( H_2^2 \)  
 e + \( H(\cdot \Sigma) \) → e + \( H(n = 2, 3) \)  
 e + \( H(\cdot \Sigma) \) → e + H^+ + e |
Table 2. Kinetics of \( \text{N}_2(X, 0 \leq v \leq 45) \) and \( \text{H}_2(X, 0 \leq v' \leq 14) \) molecules [1,2]

| e-V | 1. \( e + \text{N}_2(X, v) \Leftrightarrow e + \text{N}_2(X, w) \)  
2. \( e + \text{H}_2(X, v') \Leftrightarrow e + \text{H}_2(X, w') \)  
| \( V-V \) | 3. \( \text{N}_2(X, v) + \text{N}_2(X, w) \Leftrightarrow \text{N}_2(X, v - 1) + \text{N}_2(X, w + 1) \)  
4. \( \text{H}_2(X, v') + \text{H}_2(X, w') \Leftrightarrow \text{H}_2(X, v' - 1) + \text{H}_2(X, w' + 1) \)  
5. \( \text{N}_2(X, v) + \text{H}_2(X, v') \Leftrightarrow \text{N}_2(X, v - 1) + \text{H}_2(X, v' + 1) \)  
| \( V-T \) | 6. \( \text{N}_2(X, v) + \text{N}_2 \Leftrightarrow \text{N}_2(X, v - 1) + \text{N}_2 \)  
7. \( \text{N}_2(X, v) + \text{H}_2 \Leftrightarrow \text{N}_2(X, v - 1) + \text{H}_2 \)  
8. \( \text{N}_2(X, v) + \text{N} \Leftrightarrow \text{N}_2(X, v - 1) + \text{N} \)  
9. \( \text{N}_2(X, v) + \text{H} \Leftrightarrow \text{N}_2(X, v - 1) + \text{H} \)  
10. \( \text{H}_2(X, v') + \text{H}_2 \Leftrightarrow \text{H}_2(X, v' - 1) + \text{H}_2 \)  
11. \( \text{H}_2(X, v') + \text{N}_2 \Leftrightarrow \text{H}_2(X, v' - 1) + \text{N}_2 \)  
12. \( \text{H}_2(X, v') + \text{H} \Leftrightarrow \text{H}_2(X, v' - 1) + \text{H} \)  
13. \( \text{H}_2(X, v') + \text{N} \Leftrightarrow \text{H}_2(X, v' - 1) + \text{N} \)  
| \( h-V \) | 14. \( \text{N}_2(X, v) + \text{wall} \rightarrow \text{N}_2(X, v - 1) \)  
15. \( \text{H}_2(X, v') + \text{wall} \rightarrow \text{H}_2(X, v' - 1) \)  
| \( e-D \) | 16. \( e + \text{N}_2(X, v) \rightarrow e + \text{N}(^3\text{S}) + \text{N}(^1\text{S}) \)  
17. \( e + \text{H}_2(X, v') \rightarrow e + \text{H}(^3\text{S}) + \text{H}(^1\text{S}) \)  
| \( V-D \) | 18. \( \text{N}_2(X, v) + \text{N}_2(X, v = 45) \rightarrow \text{N}_2(X, v - 1) + \text{N}(^3\text{S}) + \text{N}(^1\text{S}) \)  
19. \( \text{H}_2(X, v') + \text{N}_2(X, v = 45) \rightarrow \text{H}_2(X, v' - 1) + \text{N}(^3\text{S}) + \text{N}(^1\text{S}) \)  
20. \( \text{H}_2(X, v') + \text{H}_2(X, v' = 14) \rightarrow \text{H}_2(X, v' - 1) + \text{H}(^3\text{S}) + \text{H}(^1\text{S}) \)  
21. \( \text{N}_2(X, v) + \text{H}_2(X, v' = 14) \rightarrow \text{N}_2(X, v - 1) + \text{H}(^3\text{S}) + \text{H}(^1\text{S}) \)  
22. \( M + \text{H}_2(X, v' = 14) \rightarrow M + \text{H}(^3\text{S}) + \text{H}(^1\text{S}) \), \( M = \text{H}_2, \text{N}_2, \text{H}, \text{N} \)  
23. \( \text{M} + \text{N}_2(X, v = 45) \rightarrow \text{M} + \text{N}(^3\text{S}) + \text{N}(^1\text{S}) \), \( \text{M} = \text{H}_2, \text{N}_2, \text{H}, \text{N} \)  
24. \( \text{N}_2(X, v \geq 14) + \text{H}_2 \rightarrow \text{N}_2 + \text{H}(^3\text{S}) + \text{H}(^1\text{S}) \)  
25. \( \text{N}_2(X, 10 < v < 25) + \text{N}_2(X, 10 < v < 25) \rightarrow \text{N}_2 + \text{N}(^3\text{S}) + \text{N}(^1\text{S}) \)  
26. \( \text{N}_2(X, 25 < v) + \text{N}_2 \rightarrow \text{N}_2 + \text{N}(^3\text{S}) + \text{N}(^1\text{S}) \)  
| R | 27. \( \text{N}(^3\text{S}) + \text{N}_{\text{wall}} \rightarrow \text{N}_2(X, v = 0) \)  
28. \( \text{H}(^3\text{S}) + \text{H}_{\text{wall}} \rightarrow \text{H}_2(X, v' = 0) \)  

Other possible mechanisms of the formation and loss of the VEM can be the radiative transitions from higher-lying singlet levels \( \text{H}_2(\text{B}^1\Sigma_u^+ \text{u}) \) and \( \text{H}_2(\text{C}^1\Sigma_u) \) [3]. Assuming that in a weakly ionized plasma they are created by electronic impact from \( \text{H}_2(\chi^1\Sigma_g^+) \) and are lost mainly through radiation (for \( \text{B}^1\Sigma_u^+ \) and \( \text{C}^1\Sigma_u \) the radiation lifetime is \( \sim 1 \text{ ns} \) [4]), their contribution was estimated as follows. The excitation cross-sections of the \( \text{B}^1\Sigma_u^+ \) and \( \text{C}^1\Sigma_u \) vibrational levels from \( \chi^1\Sigma_g^+ \) were presented in the form:

\[ Q_m^\lambda (\epsilon) = Q \cdot F (\epsilon / \epsilon_p) \cdot q_{nm} , \]

where \( Q \) is fixed for the given transition, \( F \) is the universal function of the ratio of the energy to its threshold value, \( q_{nm} \) is the Franck-Condon factor.

The possibility of such representation for the above-identified transitions is shown in [5]. The values of \( Q \) and the form of the function \( F \) were determined by the cross-sections of
electron-impact excitation of the $B^1 \Sigma_u^+$ and $C^1 \Sigma_u$ states from $X^1 \Sigma_g^+$, which were used in calculations. By the manner of their calculation, these cross-sections are the sum over all vibrational levels of the upper state produced from $H_2(X, v' = 0)$. The values of $q_{nm}$ were used, tabulated in work [6]. The excitation rates of different $B^1 \Sigma_u^+$ and $C^1 \Sigma_u$ vibrational levels were distributed over the $X^1 \Sigma_g^+$ vibrational levels proportionally to the probabilities of radiative transitions, which have been calculated using values of $q_{nm}$ and transition forces from [4]. Apparently, when the cascade transitions are included in this manner, we obtain an upper estimate because the reabsorption of radiation is ignored.

4. Main results

The values of the some plasma characteristics, the effective vibrational temperatures of $N_2(X)$ and $H_2(X)$ molecules measured in experiment and calculated according to the model are presented in table 3 as a function of initial gas composition. Notice that at the other fix plasma parameters the wall temperature depended on gas composition very slightly and was equal near 380 K. The electron density varied within $(2.4-2.67) \times 10^{16}$ cm$^{-3}$. The accuracy of determination of vibrational temperature depended on an error of intensity measurement and error of numerical method and was by our estimations $\pm 25 \%$.

**Table 3.** Some experimental and calculated results for $xN_2:H_2$ plasma under the conditions:

$P = 266$ Pa, $I_d = 50$ mA, $Q - 2.0$ cm$^{-3}$/s (STP), $R_m = 0.75$ cm

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<th>$T^{exp}_V N_2(X)$ K</th>
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The vibrational distribution functions of $N_2(X)$ and $H_2(X)$ molecules calculated according to the model are presented in figure 1 as a function of initial gas composition.

The calculation results revealed the following. Similar to the case of hydrogen plasma, the $V$-$T$ relaxation on H atoms is the main process of loss of VEM of $H_2(X)$. Because the concentration of H atoms is higher in a mixture plasma than in the $H_2$ plasma [2,7], other things being equal, the effective vibrational temperatures prove to be lower, and about 90% of molecules are concentrated on the zero vibrational level (Fig. 1).
Figure 1. Vibrational distribution functions of $N_2$ and $H_2$ in mixture plasma

$xH_2-N_2$ mixture
$P=266$ Pa, $I=50$ mA

$N_2$
- $100\%$
- $98\%$
- $80\%$
- $60\%$
- $40\%$
- $20\%$

$H_2$
- $2\%$
- $40\%$
- $60\%$
- $90\%$
- $100\%$

Vibrational quantum number

Vibrational quantum number
Owing to the large difference of energies in one-quantum transitions, the transfer of a vibrational energy from H\(_2\)(X) to N\(_2\)(X) is more effectively. Thus, additional channel of population of vibrational levels N\(_2\)(X) and de-population of H\(_2\)(X) is appeared. This situation is always kept, excepting the highest vibrational levels H\(_2\)(X, \(v' > 9\)). Relaxation of vibrational energy at the low-lying vibrational levels of H\(_2\)(X) at collisions with N\(_2\)(X) also reduces value of effective vibrational temperature against observable one in hydrogen plasma. The radiative transitions from higher-lying singlet levels H\(_2\)(B\(^1 \Sigma^+_u\)) and H\(_2\)(C\(^1 \Sigma^-_u\)) results in sharp reduction of a slope in middle part of VDF (Fig. 1).

Similar to nitrogen plasma, the population of low-lying vibrational levels of N\(_2\)(X) is defined by the electron impact pumping and by the processes of V-V exchange in N\(_2\)-N\(_2\) and N\(_2\)-H\(_2\) collisions. With increasing the H\(_2\) percentage the electron density is increased insignificantly, while total rate coefficient of e-V pumping from a zero level of N\(_2\)(X), \(\sum_{v'=4}^8 k_0\), is increased nearly twofold. It is the reason, why the vibrational temperature of N\(_2\)(X) is also increased nearly twofold (Tab. 3). The experimental results were in good agreement with calculated values except the point 10% of H\(_2\). The reason of that is not clear and further investigations are required.

The rate coefficients of V-T relaxation of N\(_2\)-H\(_2\) exceed by more than an order of magnitude the respective rate coefficients for the N\(_2\)-N\(_2\) collisions. This results in a reduction of the extent of the characteristic plateau in the distribution and in a sharp decrease of the population of high-lying vibrational levels as compared to nitrogen plasma and, as a result, to the suppression of dissociation of N\(_2\) molecules via vibrational continuum.

References


