Electron-Vibrational Energy Exchange in Nitrogen-Containing Plasma: a Comparison Between an Analytical Approach and a Kinetic Model

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Abstract This paper investigates the electron-vibrational (e-V) energy exchange in nitrogen-containing plasma, which is very efficient in the case of gas discharge and high speed flow. Based on Harmonic oscillator approximation and the assumption of the e-V relaxation through a continuous series of Boltzmann distributions over the vibrational states, an analytic approach is derived from the proposed scaling relation of e-V transition rates. A full kinetic model is then investigated by numerically solving the state-to-state master equation for all vibrational levels. The analytical approach leads to a Landau-Teller (LT)-type equation for relaxation of vibrational energy, and predicts the relaxation time on the right order of magnitude. By comparison with the kinetic model, the LT-type equation is valid in typical electron temperatures in gas discharge. However, the analytical approach is not capable of describing the vibrational distribution function during the e-V process in which a full kinetic model is required.

Keywords: electron-vibrational process, vibrational energy, relaxation time, vibrational distribution function

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1 Introduction

Modeling of nitrogen vibrational energy transfer plays an important role in describing the gas discharge physics and high speed reentry flows [1]. In both situations, the vibrational degree of the nitrogen molecule is excited to a highly non-equilibrium state. The loaded energy in the vibrational level relaxes in competing processes such as the electron-vibrational (e-V) process, vibrational-vibrational (V-V) process, vibrational-translational (V-T) process, electronic-vibrational (E-V) process, chemical-vibrational (Chem-V) process etc. Among the above processes, the e-V mechanism should be considered in nitrogen-containing plasma with an ionization degree of about $10^{-6}$ or more, because the following process of electron-impact vibrational excitation is very efficient:

$$e + N_2(X^1\Sigma_g^+,\nu) \rightarrow e + N_2(X^1\Sigma_g^+,\nu_1)$$

The pioneering work in this area was done by Lee [2] in studying non-equilibrium-ionizing high temperature flow fields. For the first time, Lee derived a Landau-Teller (LT)-type equation for the vibrational energy relaxation rate, although he pointed out that the LT condition of only allowing transition between adjacent vibrational levels was not valid. The LT-type equation was easily incorporated into more complex flow codes. Later on, Bourdon and Vervisch [3,4] presented analytical expressions for the relaxation rate using a similar model for cut-off harmonic oscillator (HO) and Morse oscillator approximations. At about the same time, Mertens [5] gave a computational model by numerically integrating the state-to-state master equation with time. However, due to missing accurate data for rate coefficients, he used scaling relations to expand the ab initio results by Huo et al [6]. The limitation of such scaling relations is that they only hold for low vibrational level $v$ and transitions with small quantum jumps $|v - w|$. Recently, Laporta et al. [7,8] obtained a complete set of cross sections (and rate coefficients) using accurate potential energy curves of nitrogen. They carried out the temporal study of vibrational energy and vibrational distribution function (VDF) using a state-to-state approach [9]. Heritier et al. [10,11] also used the above data set [8] and compared the LT-type relaxation time of different models.

Unlike previous reports, this paper attempts to study the physical mechanism of using the LT-type equation to account for electron-vibrational exchange. The idea is to compare a full kinetic model with new theoretical rate coefficients for all 58 vibrational levels, and a simple analytic approach which leads to the LT-type equation. The paper is organized as follows: after looking at
the complete dataset by Laporta et al. and the previous result by Huo et al., an empirical law is proposed for transition rates. Then, an analytical approach based on HO approximation is given and compared to that of the full kinetic model. The validity of the LT-type relaxation equation for an e-V process is also discussed with respect to time derivative of normalized vibrational energy. At last, the “bimodal” structure of VDF observed in the experiment is confirmed in our full kinetic model.

2 Theoretical model

2.1 Analytical approach

The e-V kinetics is considered on the condition of a nitrogen gas immersed in a free electron heat bath with constant temperature $T_e$. The kinetics of each vibrational level is described by a master equation considering all e-V processes allowed in Eq. (1).

$$\frac{dN_v}{dt} = n_e \sum_{w \neq v} (k_w \rightarrow v N_w - k_v \rightarrow w N_v),$$

where $v$ and $w$ are the initial and final vibrational level respectively, $k_w \rightarrow v$ is the rate coefficient for electron-impact nitrogen vibrational excitation ($w > v$) or de-excitation ($w < v$), $N_v$ is the number density of nitrogen molecule on vibrational level $v$, and $n_e$ is electron density. Then the electron-vibrational energy exchange $Q_{eV}$ is determined by multiplying Eq. (2) with energy gap,

$$Q_{eV} = \frac{1}{2} \sum_n \sum_m n_v (k_{m \rightarrow n} N_m - k_{n \rightarrow m} N_n) (E_n - E_m),$$

where $E_n$ is the energy of vibrational level $n$. The analytical approach assumes HO approximation of vibrational levels $E_n = n \hbar \nu$, where $\hbar \nu = 0.288$ eV is the vibration quanta of nitrogen molecule. The e-V relaxation process is assumed to channel through a continuous series of Boltzmann distributions over the vibrational states, so the number density of level $n$ during e-V relaxation is

$$N_n = N_0 \exp(-E_n/k_B T_v(t)),$$

where $k_B$ is the Boltzmann constant and $T_v(t)$ is the characteristic vibrational temperature of the Boltzmann distribution at time $t$. The associated de-excitation rate coefficients are derived from excitation rate coefficients using a detailed balance principle. Combining the above assumptions, Eq. (3) is written as

$$Q_{eV} = n_e n_v \hbar \nu (1 - \exp(-\hbar \nu/k_B T_v)) \sum_n \exp(-\hbar \nu/k_B T_v) \times \sum_{m > n} k_{m \rightarrow n} \exp \left( \frac{(n-m)\hbar \nu}{k_B T_v} \right) \left(1 - \exp \left( \frac{(n-m)\hbar \nu}{k_B T_v} \right) \right) (m-n),$$

where $\tau_{eV} = (n_e k_{1 \rightarrow 0})^{-1}$ is the characteristic relaxation time. For the situation of $T_e < 5000$ K, the energy exchange term is derived using a similar technique

$$Q_{eV} = \frac{n_e n_v k_{1 \rightarrow 0}}{1 - \exp(-\hbar \nu/k_B T_v)} \times \left( \bar{\nu} \exp(-\hbar \nu/k_B T_v) - \varepsilon_{vib}^{eq} \right).$$

Then a scaling relation of rate coefficients is needed to simplify Eq. (5). By referring to previous data of Huo et al. and the more recent data of Laporta et al., the following empirical law of multi-quanta transition is proposed (for details see appendix):

$$k_{m > n \rightarrow n} = \begin{cases} k_{n+1 \rightarrow n} / (m - n), & T_e \geq 5000 \text{ K} \\ k_{n+1 \rightarrow n}, & T_e < 5000 \text{ K} \end{cases}.$$

For transition between adjacent levels, Gordiets et al. [12] proposed the following scaling relation: $k_{v \rightarrow v+1} = k_{0 \rightarrow 1} / (1 + \alpha v)$, $\alpha \approx 0$. Employing the above scaling relations for $T_e \geq 5000$ K, Eq. (5) is simplified as

$$Q_{eV} = n_e n_v k_{1 \rightarrow 0} (\bar{\nu} - \varepsilon_{vib}^{eq})$$

where $\bar{\nu} = \exp(\hbar \nu/k_B T_v(t)) - 1$ is the mean vibrational energy per molecule with HO approximation and $\varepsilon_{vib}^{eq} = \frac{\exp(\hbar \nu/k_B T_v) - 1}{\exp(\hbar \nu/k_B T_v)}$ is the mean vibrational energy at equilibrium when the vibrational temperature equals to the electron heat bath temperature. Recall that the vibrational energy relaxation rate during the e-V process equals to the electron-vibration energy exchange term

$$d(n_v \bar{\nu})/dt = -Q_{eV}.$$  

This makes it possible to derive a closed equation for the mean vibrational energy in the LT-type:

$$\frac{d\bar{\nu}}{dt} = -\frac{(\bar{\nu} - \varepsilon_{vib}^{eq})}{\tau_{eV}},$$

When vibrational temperature approaches equilibrium i.e. $T_v \approx T_e$, a LT-type equation for $\bar{\nu}$ leads to a relaxation time $\tau_{eV} = (n_e k_{1 \rightarrow 0})^{-1} (1 - \exp(-\hbar \nu/k_B T_v))$. However, in general situations during the relaxation process, the definition of characteristic relaxation time is not applicable, which will be discussed within the framework of a full kinetic model as follows.

2.2 Kinetic model

The full kinetic state-to-state model relies on solving a complete set of Eq. (2) based on rate coefficients of all vibrational levels below the dissociation limit. It is more convenient to write Eq. (2) into a matrix formalism

$$\frac{d}{dt} [n_v] = [M] [n_v], M_{vw} = \begin{cases} n_e k_{w \rightarrow v}, & w \neq v \\ -n_e \sum_{u \neq v} k_{u \rightarrow w}, & v = w \end{cases}.$$
Eq. (11) constitutes a set of ordinary differential equations, and the solutions of VDF can be obtained if the matrix elements are known

$$[n_v] = \sum_k \alpha_k \exp(\lambda_k t) \left[ V_k \right],$$

where $\lambda_k$, $V_k$ are the eigenvalue and corresponding eigenvectors of $[M]$, and $[\alpha_k] = [V_k]^{-1} [n_v]_{t=0}$ is determined by the initial condition of VDF. The mean vibrational energy during the relaxation process is then calculated from the VDF in Eq. (12)

$$\varepsilon_{vib} = \sum_k \varepsilon_k \alpha_k \exp(\lambda_k t) \left[ V_k \right] / \sum_v n_v. \tag{13}$$

The relaxation rate of vibrational energy is calculated by differentiating Eq. (13) with time

$$\frac{d\varepsilon_{vib}}{dt} = \sum_k \varepsilon_k \alpha_k \lambda_k \exp(\lambda_k t) \left[ V_k \right] / \sum_v n_v. \tag{14}$$

It can be seen from Eq. (14) that the relaxation rate is in character dependent on time. In general, the e-V process does not exactly follow the LT-type equation, and a global parameter of the characteristic relaxation time in not applicable to characterize the system in the whole time range. Despite this, the use of relaxation time allows an accurate description of the vibrational energy rate change for short times in the early stage of the e-V process [13].

3 Results and discussion

Fig. 1 shows the characteristic relaxation time versus electron temperature with an electron density $n_e=2\times10^{12}$ cm$^{-3}$ from the analytic model and other LT-type value from publications. To make a direct comparison with Lee's model, all the initial vibrational temperatures are assumed to be about zero. The used rate coefficients involving 58 vibrational levels are taken from the \textit{physlet} database [14]. As can be seen, our model generally follows the tendency of results from others, and it is closer to that of Bourdon et al. The predicted relaxation time is also compared to experiment results based on low pressure nitrogen discharge [15] in which two groups of data were given: (a) $n_e = 7 \times 10^{11}$ cm$^{-3}$, $T_e = 9950$ K, $p = 1.4$ Torr, $\tau = 200$ $\mu$s; (b) $n_e = 5.9 \times 10^{11}$ cm$^{-3}$, $T_e = 9700$ K, $p = 0.7$ Torr, $\tau = 230$ $\mu$s. If the rate coefficients $k_{1\rightarrow 0} = 8 \times 10^{-9}$ cm$^3$ s$^{-1}$, the theoretical relaxation time for group (a) and (b) are 179 $\mu$s and 212 $\mu$s respectively, and they agree well with the experimental results. The simple analytical approach proposed in section 2.1 can give reasonable accuracy for relaxation time, and explain its dependence on electron density, electron temperature and chamber pressure in gas discharge experiments.

Fig. 2(a)-(d) shows the mean vibrational energy versus the normalized time during the e-V process, while the solid line presents the analytic approach and the dashed line presents the full kinetic method. The initial VDF is assumed to be a Boltzmann distribution with room temperature $T_e = 300$ K, and constant temper-atures of the electron heat bath are 2000 K, 4000 K, 8000 K and 10000 K in Fig. 2(a)-(d) respectively. For different electron temperatures, all relaxation times are normalized to the corresponding characteristic relaxation time in Eq. (9) $T^n = t/\tau_{eV}$. At both $T_e < 5000$ K (in Fig. 2(a) and (b)) and $T_e \geq 5000$ K (in Fig. 2(c) and (d)), the results of the analytical approach agree well with those from the kinetic model, although they do not perfectly match at $T_e = 2000$ K. The comparison above shows that the vibrational energy relaxation during the e-V process can be simply described using HO approximation and the assumption of the e-V relaxation through a continuous series of Boltzmann distributions over the vibrational states, by observing the scaling relation of transition rates. This conclusion encourages the use of the LT-type equation in describing the electron-vibrational energy exchange in nitrogen-containing plasma, while a similar technique has been adopted in the study of high speed flows for a long time.
Fig. 3 shows the normalized time derivative of vibrational energy as a function of normalized vibrational energy $e_{\text{vib}}^n = e_{\text{vib}} / e_{\text{vib}}^{0}$ for different electron temperatures. The solid straight line plots the LT-type as a reference, while $de_{\text{vib}}^n/dt^n \sim e_{\text{vib}}^n$ shows a linear dependence and the slope is inversely proportional to the characteristic relaxation time. The deviation from linearity was observed to be lower than 40% in the full kinetic model in the electron temperature range between 8000 K and 20000 K. When electron temperature is lower than 5000 K, although quasi-linearity holds for $de_{\text{vib}}^n/dt^n \sim e_{\text{vib}}^n$, the slope of the curve is slightly larger than that of the analytical LT-type (actually if time normalization is according to Eq. (10) for $T_v \approx T_e$, better agreement between the analytical approach and the kinetic model is obtained). When the electron temperature is higher than 30000 K (results not shown in Fig. 3), the curvature of the $de_{\text{vib}}^n/dt^n \sim e_{\text{vib}}^n$ relation basically rejects a LT-type approach. In general, the analytical LT-type approach is not valid when the electron temperature is either too low or too high. A possible reason is that incident electrons within those energy ranges are not efficient to excite vibrational levels \[16\]. Instead, they favor rotational level excitation or electronic level excitation \[17\], and the observed scaling relation for e-V transition does not hold anymore.

![Fig. 3](image_url)

**Fig. 3** Normalized time derivative of vibrational energy versus normalized vibrational energy for different electron temperatures (the solid line of LT-type is plotted as a reference)

Fig. 4 shows the VDF of the first 10 vibrational levels $v=0-10$ during the e-V process for a full kinetic model (VDF is normalized to the $N_{v=0}$ on the initial condition, time is normalized to the characteristic relaxation time). The initial VDF is a Boltzmann type with $T_v=300$ K (the VDF versus the vibrational level is a straight line in a semi-logarithmic plot when $t^n=0$), and the electron heat bath is 10000 K. Although the relaxation of vibrational energy can be described by the analytical LT-type model on the above condition (as shown in Figs. 1-3), the relaxation of VDF differs from the assumption of the e-V relaxation through a continuous series of Boltzmann distributions over the vibrational states. In fact, the VDF shows two segments during normalized time between 0.001 to 0.1, corresponding to a low vibrational temperature $T_v^{01}$ and a high vibrational temperature $T_v^{1v}$.

\[
T_v^{01} = \frac{E_1 - E_0}{k_B \ln(N_0/N_1)}, \quad T_v^{1v} = \frac{E_v - E_1}{k_B \ln(N_1/N_v)}. \tag{15}
\]

When normalized time is larger than unity ($t^n=1$ and 10), the relaxation process is channeled through the Boltzmann distribution. The result of the full kinetic model is similar to the typical “bimodal” structure reported in nitrogen discharge \[18\,19\].

![Fig. 4](image_url)

**Fig. 4** Vibrational distribution function at different time points during the e-V process (VDF is normalized to the $N_{v=0}$ on initial condition, time is normalized to characteristic relaxation time)

## 4 Conclusions

In conclusion, the electron-vibrational energy exchange is studied in nitrogen-containing plasma by both an analytical approach and a kinetic model. Based on HO approximation and the assumption of the e-V relaxation through a continuous series of Boltzmann distributions over the vibrational states, the relaxation of vibrational energy is LT-type by the proposed scaling relation of transition rates. The LT-type analytical approach is found to be valid in the electron temperature range between 5000 K and 20000 K with reasonable accuracy by comparison with the full kinetic model. However, it is not correct to describe the time evolution of the VDF with the analytical approach. The kinetic model shows that the e-V process is channeled through a “bimodal” structure of VDF.

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## Appendix

Because a large number of rate constants are required in describing the e-V energy exchange, it is quite common to look for scaling relations of transition rates.
Referring to the recent \textit{ab initio} data \cite{9}, a scaling relation is proposed in Eq. (6). Fig. A1 presents the calculated data \cite{14} (scattered points) and the scaling relation (solid lines) for rate constants $k_{v-0}$. When $T_e < 5000$ K (the left of the dashed grey line in Fig. A1), the calculated rate constants for different vibrational levels approach each other at the same electron temperature; when $T_e > 5000$ K (the right of the dashed grey line in Fig. A1), the scaling relations agree with calculated results with reasonable accuracy for vibrational levels lower than 5. Transition rates with large vibrational jumps are not shown, and are believed to induce considerable errors using scaling relations \cite{9}. However, for typical conditions of gas discharge physics, scaling laws were proposed \cite{3-5,13} and may allow for simple analytical solutions.

![Fig.A1 Rate constants $k_{v-0}$ as a function of electron temperature for different vibrational levels: scattered points are calculated ab initio results \cite{14}, and solid lines are scaling relations](image)

**References**

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