The Harmonic and Anharmonic Models for Vibrational Relaxation and Dissociation of the Nitrogen Molecule

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The theory of the vibrational energy relaxation and dissociation of the nitrogen molecule is formulated. The appropriate rates are developed for the harmonic (HO) and anharmonic oscillator (AHO) models. Specifically, a V-T rate for $T < 2000 \text{K}$ is recommended. Comparison is made in the rates of the HO and AHO models indicating that relaxations in the AHO model is more rapid compared to that of the HO model.
CONTENTS

1. Introduction ......................................................................................................................... 1
2. The Master Equation ............................................................................................................. 3
3. Rate Coefficients ................................................................................................................ 4
   3.1 Electron Impact Excitations of the Vibrational Levels ..................................................... 4
   3.2 The V-T Rate Coefficients ............................................................................................. 5
   3.3 The V-V Transition Rates ............................................................................................... 8
   3.4 Rate Coefficient Comparisons ...................................................................................... 10
4. Dissociation and Recombination ......................................................................................... 11
5. Discharge Model .................................................................................................................. 12
References ............................................................................................................................... 13
1. INTRODUCTION

In electric, microwave, laser and electron beam initiated discharges in nitrogen, a fair portion of the input energy is stored in the $N_2$ vibrational mode. In discharges where the average electron energy is below 2 eV approximately 80% of the energy is stored in the vibrational levels. This stored energy has two interesting channels for its dissipation, which are the dissociation of the molecule and the vibrational relaxation into thermal energy. However, when the vibrational states have radiative channels, the vibrational energy is dissipated by radiative means also.

The energy storage and the development of the vibrational distribution in nitrogen discharges occur as a result of the electron-molecule, and molecule-molecule collisions. The electron-molecule collisions hereafter called the e-V processes, populate various vibrational levels of the molecule. However, the molecule-molecule collisions are of two types. One of these, hereafter called the V-T process, transfer energy from the vibrational mode to the kinetic energy and vice versa. The other type is the V-V collisions where a vibrational quanta is exchanged between the collision partners. Under V-V collisions energy is also exchanged between the vibrational and kinetic modes when the vibrational energy levels are anharmonic in nature.

Theoretical studies of the vibrational kinetics in nitrogen, other diatomic molecules and molecules diluted in atomic species, have been numerous. These studies were stimulated by interest in the relaxation
phenomena and its rate in laboratory discharges,\(^3,4,6,10,11\) molecular lasers,\(^7,9\) chemical reactions, molecular dissociation and recombination and ionspheric molecules.\(^5\) In these studies harmonic\(^2,13\) or anharmonic\(^3-12\) oscillator models were utilized and a master equation in general, was solved largely under steady state conditions, with the main interest in V-T and V-V processes. Recent studies\(^9,11,13\) have included the electron-molecule collisions and time dependent master equations have been solved numerically. However, even when time dependent solutions\(^12\) of the master equation were obtained, one or more temperatures, i.e., the electron and the gas temperatures were kept constant. Such approaches may be appropriate for a low degree of ionization and low vibrational temperatures. Therefore, a self-consistent approach, where the various temperatures are calculated simultaneously with the master equation, is desirable. In this manner the energy flow from one mode to another is accounted for and its effects on the rate coefficients and relaxation times will be manifested as a matter of course.

In this paper we discuss the theory of the vibrational relaxation in \(N_2\). We discuss the physics of two models, a harmonic oscillator (HO) and an anharmonic oscillator (AHO), develop the appropriate rate coefficients and delineate their behaviour. Specifically we develop a V-T rate coefficient for temperatures below 2000 °K where the deactivation rate is much different from that obtained from extending the rates based on the high temperature\(^14\) relaxation data. Such a model where various temperatures are treated self consistently should be useful for channel expansions after energy depositions and provide the tool for infrared emissions calculations where radiatively active molecules (\(CO_2\), NO, \(NO_2\) and \(N_2O\)) react with the vibrationally excited \(N_2\) molecules.
2. THE MASTER EQUATION

The master equation which governs the population density of the v-th vibrational level $N_v$, in an electric, laser or microwave initiated discharge in $N_2$ is

$$\frac{dN_v}{dt} = \sum_{w=1}^{v+1} N_{v+1} N_{w-1} P_{v+1,v}^{w-1,w} - \sum_{w=1}^{v+1} N_{v,w} P_{w,v,v+1}^{v,w,w-1}$$

$$- \sum_{w=0}^{v-1} N_{v,w} P_{v-1,v,w}^{w,v,w+1} + \sum_{w=0}^{v-1} N_{v-1,w} P_{v-1,v,w}^{w+1,w}$$

$$+ N \sum_{w} N_{v,w} X_{wv} - N \sum_{v} N_{v,w} Y_{vw}$$

$$- M \sum_{v} N_{v,w} R_{v,v+1} + M \sum_{w} N_{v,w} S_{w,w,w-1}$$

(1)

where the appropriate processes are: the electron molecule and the molecule-molecule collisions. The electron molecule collisions comprise excitation and deexcitation of the vibrational levels, i.e.,

$$e + N_v \rightarrow e + N_v$$

(2)

where the excitation and the deexcitation rate coefficients are designated by $X_{wv}$ and $Y_{vw}$, respectively. In a V-V collision i.e.

$$N_{v+1} + N_{w-1} \rightarrow N_v + N_w$$

(3)

a molecule at the $v+1$ level loses one vibrational quanta and descends to level $v$ while the molecule at the $w-1$ level gains a quanta and ascends to level $w$. The rate coefficient for this process is designated by $P_{v,v+1,w}^{w-1,w}$ and the corresponding inverse process is obtained by the principle of the detailed balance.
In a V-T collision i.e.,

\[ M + N_w \rightarrow N_{w-1} + M \]  \hspace{1cm} (4)

a molecule exchanges a vibrational quanta with the thermal reservoir comprising \( M \) molecules. The rate coefficient for the V-T deactivation is designated by \( S_{w,w-1} \) while the corresponding excitation is given by \( R_{v,v+1} \) and is obtained by detailed balance.

The number of vibrational levels represented by the master equation depends on the model. The HO model with equal energy spacings between the vibrational levels of 0.29 eV (see Ref. 15) results in 34 bound levels while the AHO model has 46 bound levels. The energy of the \( v \)-th vibrational level, \( E_v \), is

\[ E_v = 0.29 \left[ (v + \frac{1}{2}) - \delta (v + \frac{1}{2})^2 \right] \]  \hspace{1cm} (5)

where \( \delta \) is the adiabaticity constant with a value of 0.006 (see Ref. 15).

3. RATE COEFFICIENTS

3.1 ELECTRON IMPACT EXCITATIONS OF THE VIBRATIONAL LEVELS

The electron impact rate coefficients for the vibrational excitation can be obtained from the measured cross sections.\(^{16,17}\) These cross sections for transitions from \( v=0 \) to \( v=8 \) have been averaged\(^{18}\) with the electron velocity over a Maxwellian velocity distribution and the corresponding coefficients are shown in Fig. 1. As for excitation between and to levels above \( v=8 \) we utilize the often used\(^{19}\) relation.

\[ X_{v,v+\Delta v} = X_{0,\Delta v} \]  \hspace{1cm} (6)
The electron de-excitation rate coefficient $Y_{v,w}$ is obtained from the corresponding excitation by the principle of detailed balance. The rates used for the harmonic oscillator are shown in Fig. 1. On the other hand, for the AHO the individual excitation rates should be multiplied by an exponential whose exponent is given by the energy defect ($\Delta E_d = 0.29v - E_v$) divided by the electron temperature.

3.2 THE V-T RATE COEFFICIENTS

For the harmonic oscillator the V-T rate coefficient, $S_{v,v-1}$, is related to the de-excitation rate of the $v=1$ state, $S_{10}$, and the harmonic oscillator relation, i.e.,

$$S_v + \Delta v, v = (v+\Delta v) S_{10} \tag{7}$$

The V-T excitation rate coefficient is

$$R_{v,v+\Delta v} = (v+\Delta v) S_{01} \tag{8}$$

and $S_{01}$ is related to $S_{10}$ via detailed balance, i.e.

$$S_{01} = S_{10} \exp\left(-\frac{0.29}{kT}\right) \tag{9}$$

where $T$ is the gas temperature.
For the AHO, on the other hand, the V-T de-excitation rate is

\[ S_{v,v-1} = Z P_{VT} T \left[ \frac{v}{1-\delta v} \right] F(x_{v,v-1}) \]  

(10)

here \( \delta \) is the adiabaticity constant, \( F(x_{v,v-1}) \) the adiabaticity factor which can be approximated\(^3\) by

\[ F(x_{v,v-1}) = \frac{1}{2} \left[ 3 - \exp(-2X/3) \right] \exp(-2X/3) \]  

(11)

where

\[ x_{v,v-1} = \left( \frac{1}{2} \right)^{3/2} \left( \frac{\dot{\epsilon}}{T} \right) \frac{1}{2} \left[ 1 - 2\delta v \right] \]  

(12)

and \( \dot{\epsilon} = 5.38 \times 10^6 \) for \( N_2 \) (see Ref. 20). In Equation (10) \( Z \) is the rate coefficient for the collision of two hard spheres where

\[ Z = \pi d^2 \frac{(8kT)}{2 \mu} \frac{1}{2} = 1.7 \times 10^{-11} \sqrt{T} \]  

(13)

Here, \( d \) is the diameter of the molecule (\( d = 3.75 \) Å, see Ref. 21) and \( \mu \) is the reduced mass. \( P_{VT} \) is the probability per collision that energy is exchanged. In order to obtain this probability we must relate the deactivation rate (Eq. 10) to the measured relaxation times, \( \tau \), where \( P \) is the pressure, generally in units of one atmosphere at room temperature. The experimental data compiled by Millikan and White\(^{14}\) for \( \tau \), shown in Fig. 2, is valid for \( T=2000-9000^\circ K \) and can be expressed as \( 4.2 \times 10^{-12} \exp (234.9T^{-1/3}) \).

However, data below \( T=2000K \), not given by Milliken and White\(^{14}\), do not fall on this straight line on a log plot vs. \( T^{-1/3} \). This merits further discussion.
The most recent room temperature data of $p_T$ by Kovacks and Mack\textsuperscript{22} yields a value of $(4 \pm 1)$ atm/sec. Other data below $T = 2000^\circ K$ are those by Henderson\textsuperscript{23} ($T = 2000^\circ K$) which yields $p_T = 1$ atm/sec and those of Huber and Kantrowitz\textsuperscript{24} ($T = 550 - 760^\circ K$), Lukasik and Young\textsuperscript{25} ($T = 770, 1020$ and $1186^\circ K$), and Hurle\textsuperscript{26}. These experimental data are shown in Fig. 2 along with the theoretical calculations of Benson and Berend\textsuperscript{27}. These calculations\textsuperscript{27} give the probability for $v = 1 \rightarrow 0$ deactivation in nitrogen which fits the high temperature region very well. Below $T = 2000^\circ K$ the $p_T$ values from these calculations\textsuperscript{27} (shown in Figure 2) indicate that the $p_T$ curve in reality can be divided into two regions. One for $T \geq 2000^\circ K$ and another for $T \leq 2000^\circ K$ where a fit with a different slope is in order. We suggest the following fits

$$p_T = 4.2 \times 10^{-12} \exp(234.9 T^{-1/3})$$

(14a)

for $T = 2000 - 9000^\circ K$ and

$$p_T = 4.5 \times 10^{-8} \exp(120.3 T^{-1/3})$$

(14b)

for $T = 300^\circ - 2000^\circ K$. This last fit differs by many orders of magnitude from the extension of the high temperature data to below $2000^\circ K$. Utilizing these relations we obtain the following expressions, for the vibrational translational deactivation rate coefficients,

$$S_{v,v-1} = \frac{3.23 \times 10^{-11} \ T \exp(-234.9 \ T^{-1/3})}{(1-e^{-\chi/T}) \ F(\chi = 800)} \ \frac{(\frac{v}{1-\delta v})}{\sqrt{T}} \ F(\chi_{v,v-1})$$

(15a)
For $T = 2000 - 9000^\circ K$ and

$$S_{v,v-1} = \frac{3.02 \times 10^{-15} \exp \left(-120.3 \frac{T}{T^{1/3}}\right) T}{(1-e^{-8/T}) F \left(\frac{\gamma}{\sqrt{T}}\right) \frac{\nu}{[1-\delta\nu]} F (\nu, \nu-1)} (15b)$$

for $T = 300 - 2000^\circ K$.

### 3.3 THE V-V TRANSITION RATES

To develop the appropriate rates we start with the probability of energy exchange per collision derived by Rapp and Englander-Golden.\textsuperscript{28} This probability is\textsuperscript{4,28}

$$A_{sm}^{rn} = \sin^2 \left(\frac{4\pi \nu L V_0 U_{rn} U_{sm}/h}{4L E_d}\right) \frac{2L E_d}{V_0} \text{Sech}^2 \left(\frac{2L E_d}{V_0}\right) (16)$$

where $E_d$ is the energy defect, $V_0$ the relative velocity, $\mu$ the reduced mass of the collision partners and $L = 0.2$ $\text{A}$ for $N_2$, which is a characteristic length\textsuperscript{5} in the exponential of the repulsive interaction potential. $U_{rn}$ is the matrix element for the harmonic oscillator with

$$\left(U_{01}\right)^2 = \frac{1}{4L} \frac{h}{\pi M_0 v} \quad (17)$$

Here, $M_0$ is the reduced mass of an oscillator and $v$ is the vibrational frequency. For HO the energy defect is zero and the $\sin^2$ term in Eq. 16 can be approximated\textsuperscript{5} by the square of its argument. This results in

$$A_{01}^{10} = 3.8 \times 10^{-6} \ T \quad (18)$$
Hence the V-V exchange rate coefficient is

\[ p_{01}^{10} = 6.45 \times 10^{-17} (T)^{3/2} \] (19)

where we have utilized the collision rate coefficient (see Eq. 13). For arbitrary levels, one has

\[ p_{v+1,v}^{w+1,w} = (v+1) p_{01}^{10} \] (20)

and

\[ p_{v,v+1}^{w-1,w} = w(v+1) p_{01}^{10} \] (21)

However, for AHO, the V-V exchange rate is

\[ p_{v,v-1}^{w-1,w} = Z p_{v,v} T \left[ \frac{v}{1-\delta v} \right] \left[ \frac{w}{1-\delta w} \right] F(Y_{v,v-1}^{w-1,w}) \] (22)

where \( Z \) is the collision rate coefficient, \( P_{v,v} \) the probability for energy exchange, and \( F(Y_{v,v-1}^{w-1,w}) \) is given by Eq. (11), however, its argument is defined by

\[ Y_{v,v-1}^{w-1,w} = 10.19 \left[ \frac{v-w}{(T)^{1/2}} \right] \] (23)

Using the expression for \( Z \) and Eqs. (19) and (22) we obtain

\[ p_{v,v-1}^{w-1,w} = 6.5 \times 10^{-17} (T)^{3/2} \left[ \frac{v}{1-\delta v} \right] \left[ \frac{w}{1-\delta w} \right] F(Y_{v,v-1}^{w-1,w}) \] (24)
3.4 RATE COEFFICIENT COMPARISONS

A comparison between various rate coefficients and their behavior with temperature is useful in delineating the impact of various processes on relaxation and dissociation. Figure 3 shows the V-T deactivation rate coefficients as a function of the vibrational quantum number for two gas temperatures of 300 and 1000 °K. Two different expressions (see Eqs. 15a and 15b) were utilized. The difference between these are quite obvious, which implies that the extension of the rates obtained from high temperature PT data to regions below 2000 °K will underestimate the vibrational deactivation rates. Also shown are the deactivation rates for the harmonic model. We observe from this figure that the deactivation rate coefficients are higher for higher quantum levels and that these rates increase with increasing gas temperature. The deactivation rates for the harmonic model increase with increasing v but at a much lower rate compared to the AHO model. In Figure 4 we show the V-V rate coefficients as a function of v for two gas temperatures of 300 and 1000 °K. Again, the V-V rates are higher for higher temperatures and in general are much higher than the V-T rate coefficients. The near resonance V-V rates increase with increasing v while V-V exchanges for the non-resonance decrease with increasing v in contrast to the linear rise shown in the HO model.

The higher rate coefficients for the AHO model compared to the corresponding coefficients for the HO model implies higher relaxation rates, which can be tested against experimental results. Furthermore, the V-T rates, especially for gas temperatures below 2000 °K could be verified by a suitable experiment.
4.0 DISSOCIATION AND RECOMBINATION

The dissociation of the nitrogen molecule in a discharge occurs through three distinct processes. If we designate the population density of the last bound state by \( N(46) \) then its dissociation rate due to V-V processes, assuming a one quantum exchange, is

\[
K_d(vv) = N(46) \sum_{v=1}^{46} P_{v,v-1} N(V)
\]  

(25)

The corresponding recombination rate is

\[
R_r(vV) = N^2 \sum_{v=0}^{46} P_{v,v+1} N(V)
\]  

(26)

Where \( N \), without a subscript, devotes the density of the nitrogen atom.

The dissociation rate due to the V-T process is

\[
K_d(vT) = N(46) M S_{46,47}
\]  

(27)

and the corresponding recombination rate, using the principle of detailed balance, is

\[
R_r(vT) = \frac{N(46) S_{46,47}}{N \cdot N} 
\]  

(28)

Finally, the plasma electron dissociation rate is

\[
K_d(eV) = N_e \sum_{v=38}^{46} N(V) N_{x,v,47}
\]  

(29)

Thus the total dissociation rate due to these three processes (e-v, V-V and VT) is
\[ K_d = K_{d(VV)} + K_{d(VT)} + K_{d(eV)} \]  \hspace{1cm} (30)

5.0 DISCHARGE MODEL

The equations describing the vibrational model can be used in two ways to study vibrational relaxation and dissociation in nitrogen. The first approach is to assume a given temperature or temperatures and an electron density and use the model to gain the appropriate understanding of the dissociation, vibrational distribution, equilibration time, and so on. The most appropriate approach, however, requires the coupling of the vibrational model into an ab initio discharge model that calculates the time development of the electron density and the various temperatures. This and more detailed studies of the vibrational energy relaxation and dissociation of \( \text{N}_2 \) will be forthcoming.
REFERENCES

Fig. 1 — Electron impact excitation rate coefficients for the eight ground state vibrational levels.
Fig. 2 — Experimental and calculated relaxation times $P_\tau$ in nitrogen: K(Ref. 22), B&B(Ref. 27), H(Ref. 23), H&K(Ref. 24), L(Ref. 25).
Fig. 3 — The vibrational-translational deexcitation rate coefficients for harmonic and anharmonic oscillators as a function of the vibrational quantum number.
Fig. 4 — The near-resonance and non-resonance vibrational-translational exchange rate coefficients as a function of the vibrational quantum number.
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