Final Report on Consortium Agreement NCA2-519

Vibration Dissociation Coupling
in Nonequilibrium Flows

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This is the final report on the Consortium Agreement NCA2-519 between North Carolina State University and the NASA Ames Research Center. The research was aimed at using the Schwartz, Slawsky, Herzfeld (SSH) theory (Ref. 1) to simulate the vibrational relaxation of nitrogen molecules undergoing dissociation or recombination over a wide range of conditions. The results of these simulations were then treated as exact, and they were used to develop a model for the coupled vibration-dissociation process. This new model is simple enough to be used in computational fluid dynamics codes, but still captures the physics of the complex process. The model is used to simulate the flow over typical geometries to test it and to determine how much impact it has on the flow field.

This work has been completed and has been reported at two national technical meetings and in a journal article. A second journal article is in preparation. One Ph.D. student, D. Brian Landrum, was supported by this work. The key elements of this research are summarized below; further details can be found in the enclosed technical papers and Ph.D. dissertation.

Improvements to the SSH Model

Much of the initial work was aimed at reproducing the work of Sharma, Huo, and Park (Ref. 2). This was not easy. A number of mistakes were made in the molecular constants and it took a lot of work to trace down these problems and to

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verify the results. One paper resulted from this work and was presented at the 1991 AIAA Reno Meeting. There were several mistakes in this paper also. (Again stemming from erroneous physical constants used in the SSH model.) These problems were fixed and the simulations re-run for the journal version of the paper, which has been published in the *Journal of Thermophysics and Heat Transfer* (Volume 6, Number 4, Oct.-Dec., 1992, pages 643-649), which is enclosed.

Results from Simulations

In this section the basic results from the SSH simulations are discussed with emphasis toward using them to develop a new model for vibration-dissociation coupling. Figures 1-3 present a selection of results using the new formulation for a heating case. In the heating case the gas is assumed to initially be in equilibrium at $T_i = 4000\,\mathrm{K}$. The initial number density of nitrogen molecules is assumed to be $N_x = 1.0 \times 10^{17}\ \mathrm{cm}^{-3}$. Using equilibrium relations the atomic number density is calculated to be $N_a = 7.58 \times 10^{14}\ \mathrm{cm}^{-3}$. The gas is instantaneously heated to $8000\,\mathrm{K}$ and allowed to relax under constant volume and temperature constraints. This process is qualitatively representative of the flow behind a normal shock wave.

Figure 1 shows single-quantum vibrational transition rates summed over all possible combinations of v_b and v_b'. There is some concern about the accuracy of the SSH rates formulated with theoretical steric factors which have often been shown to be inaccurate. Therefore, the calculated rates were corrected to match available experimental data at equilibrium. For the V-V and V-T rates the corrections are based on the $k_{0,1}$ rate as correlated by Millikan and White (Ref. 3). For dissociation the rate corrections were based on rate coefficients correlated to experimental data by Park (Ref. 4). The rates for several possible values of α are shown and compared to Landau-Teller rates. Note that for $\alpha = 1.0 \times 10^8\ \mathrm{cm}^{-1}$ an obvious rate minimum is present. With $\alpha = 3.16 \times 10^8\ \mathrm{cm}^{-1}$ they are Landau-Teller-like in the lower levels and display no local minimum. But a large disparity in the magnitudes of the upper and lower level rates has a significant affect on the vibrational relaxation.

Figures 2 and 3 illustrate the relaxation process. In Fig. 2 the time evolution of the normalized population of each level, $N(v)/N(v)_{EQ}$ is plotted. This param-

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eter is the number density of molecules in a given vibrational level divided by the number density of molecules in that level at equilibrium ($T_v = T_f$). Figure 3 shows the evolution of the population of each vibrational level normalized by the total number density of molecules, N_x. When the vibrational levels are populated according to a Boltzmann distribution, the slope of the distribution is linear and is inversely proportional to the vibrational temperature, T_v. Decreasing slopes represent increasing temperatures. It is obvious that the middle and upper levels relax through non-Boltzmann distributions. The disparity between the upper and lower level vibrational transition rate magnitudes inhibits the transfer of molecules from lower levels to the higher. But once a molecule reaches the upper levels it is quickly elevated to the uppermost levels. This behavior is coupled with the fact that the probability of dissociation is only significant in the uppermost levels. Thus the rate of dissociation is approximately balanced by the rate of molecular transfer from the lower levels.

From the explicit Master Equation simulation we have learned several important characteristics of the relaxation process:

1. Only nearest neighbor transitions contribute significantly to the vibrational relaxation. The relaxation process illustrated in Figures 2 and 3 is nearly identical whether all possible transitions or only nearest neighbor transitions are considered. This is somewhat surprising especially for the closely spaced upper vibrational levels.

2. Significant dissociation only occurs from the highest vibrational levels. Specifically, in our simulation only the top four vibrational levels were required to adequately account for dissociation and recombination.

3. The effective V-V transition rate is essentially infinite between the two highest vibrational levels. This conclusion is shown in Fig. 2 where it can be seen that there is a zero slope in the normalized population distribution between the top two levels. In other words

$$\frac{N_{v_{max}}}{N_{v_{max},EQ}} = \frac{N_{v_{max}-1}}{N_{v_{max}-1,EQ}} \tag{1}$$

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Further analysis of these simulations is made in the enclosed *J. Thermophysics and Heat Transfer* article and Ph.D. dissertation.

A New Bi-Level Model

Although useful in providing an understanding of the various aspects of the vibrational relaxation process, the full Master Equation simulation is impractical for use in reacting flow field calculations. Therefore a simple, more tractable analytic model which embodies the same physics is desirable. We have developed such a model. This model is described briefly in this section.

The SSH theory simulations show that as the nitrogen molecule undergoes vibrational relaxation, the vibrational states are distributed in a characteristic way. The lower vibrational states undergo relaxation as formulated by Landau and Teller (Ref. 5), while the upper vibrational states very rapidly attain a distribution that corresponds to the translational temperature. The upper levels adjust to the translational temperature very quickly because V-V coupling is very efficient where the energy spacing is small. The number of molecules that have high vibrational energy increases during the relaxation process due to molecules being fed up the vibrational ladder from the lower vibrational levels. The SSH theory simulations show that almost all of the the molecules that dissociate come from the highest several vibrational levels. Thus, with this in mind, we can propose a simple model that has these characteristics. Let the nitrogen molecules be divided into two types: those with low vibrational energy, N_2 and those with high vibrational energy, N_2^*. The excited molecules are the only ones that are allowed to dissociate, and their population increases due to V-T collisions that raise some of the N_2 molecules to the excited level N_2^*. This may be written as

$$N_2 + M \rightleftharpoons N_2^* + M$$
$$N_2^* + M \rightleftharpoons N + N + M,$$

(2)

where M is a collision partner. The reactions have rates that may be determined from the SSH theory simulations. The distribution of the vibrational energy in the lower energy level is characterized by the lower level vibrational temperature, $T_{v\ell}$. Assuming that the lower vibrational states of the molecule may be represented as

a truncated harmonic oscillator, an energy conservation equation may be written for the lower level vibrational energy. This equation has a form similar to that of the Landau-Teller vibrational relaxation expression (Ref. 5). The vibrational states of the excited vibrational level of nitrogen, N_2^*, are represented by a different characteristic temperature of vibration. The population distribution within this level is fixed using the fact that the distribution is governed by the local translational temperature and the population of the states adjacent to the boundary between the lower level and the excited level must be continuous. Thus, this new model requires the solution of one additional conservation equation; that of the excited state population. The rate of upper level production from the lower level (the rate governing the first reaction in Eq. (2)) is found from the SSH theory simulations. The simulations show that this rate is nearly a constant during the entire simulation if it is related to the population of the highest vibrational state within the lower level. Thus, this rate is only a function of the translational temperature, and may be computed from the SSH theory without performing any simulations.

This bi-level model satisfies all of the essential characteristics of the coupled vibration-dissociation relaxation process. All of the rates may be determined from the SSH and Landau-Teller theories. The model satisfies detailed balancing. In summary, we have represented the relaxation process with the model:

$$
\frac{dN_{N_2}}{dt} = \left(- k_{f_x} N_{N_2} F(T_{vl}, T) + k_{b_x} N_{N_2^*} \right) N_x \\
+ \left(- k_{f_N} N_{N_2} F(T_{vl}, T) + k_{b_N} N_{N_2^*} \right) N_N
$$

(3)

$$
\frac{dE_{vib}}{dt} = \frac{\left(E_{vib,EQ} - E_{vib} \right)}{\langle \tau \rangle} \\
+ \frac{k \theta_{vl} v_c}{\langle \tau \rangle} \left[\frac{N_{N_2}}{\exp(v_c \theta_{vl}/T) - 1} - \frac{N_{N_2^*} G(T)}{1 - \exp(-\theta_{vl}/T)} \right] \\
+ k \theta_{vl} v_c \frac{dN_{N_2}}{dt}
$$

(4)

$$
\frac{dN_{N_2^*}}{dt} = \left(- k_{d_x} N_{N_2^*} + k_{r_x} N_N^2 \right) N_x \\
+ \left(- k_{d_N} N_{N_2^*} + k_{r_N} N_N^2 \right) N_N \\
- \frac{dN_{N_2}}{dt}
$$

(5)

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where the total number density of molecules is

$$N_x = N_{N_2} + N_{N_2^*} \tag{6}$$

The function $F(T_{vl}, T)$ defines the population of the highest vibrational state in the the lower level $N(v_c - 1)$. This function is given by

$$F(T_{vl}, T) = \exp\left(\beta\theta_{vl}\left(\frac{1}{T_{vl}} - \frac{1}{T}\right)\right) \\ \times \exp(-(v_c - 1)\theta_{vl}/T_{vl})/Q_{vl}(T_{vl}) \tag{7}$$

The second set of exponential terms is due to the truncated harmonic oscillator representation of the lower level molecules. Here Q_{vl} is the total vibrational partition function for the lower levels. The first exponential was included to account for molecular anharmonicity. As can be seen in Fig. 2 the lower levels relax through a series of log-linear near Boltzmann distributions. The mid-levels though display populations which are extremely non-Boltzmann and much larger in magnitude. The exponential factor allows this behavior to be included. The term a function of the degree of thermal nonequilibrium as modeled by the difference in the inverses of the vibrational and translational temperatures. The β factor allows control over the degree to which this factor can modify the effective mid-level population distributions. The function $G(T)$ defines the population of the lowest vibrational state in the upper level $N(v_c)$. This function is given by

$$G(T) = \exp(-E(v_c)/kT)/Q_{vu}(T) \tag{8}$$

Here $Q_{vu}(T)$ is the total vibrational partition function for the upper level. Note that the relative populations of the states comprising the upper vibrational level are functions of the translational temperature.

The kinetic rates for vibrational excitation k_{f_x} and k_{f_N} are obtained from the full simulation. The reverse rates are calculated by detailed balance. The first term in Eq. (4) is the familiar Landau-Teller relaxation equation for the vibrational energy. The parameter $\langle \tau \rangle$ is the mole averaged vibrational relaxation time. The bracketed terms are due to truncation of the lower level harmonic oscillator. These two terms along with the first represent redistribution of vibrational quanta among

the states of the lower level. The last term is the removal of vibrational energy by excitation of N_2 to N_2^*. Equation (5) is the rate of change of the population in the upper level. This includes terms which account for dissociation and recombination and a term representing production of N_2^* molecules by excitation of N_2. The kinetic dissociation rates k_{d_a} and k_{d_N} are also obtained from the full simulation. Recombination rates are calculated by detailed balance. Note that with this bi-level model formulation the vibrational energy removed by dissociation is characteristic of the highest vibrational levels and not the average energy often used in the TT_v model.

Results from Bi-Level Model

The bi-level model described above has been used to simulate the relaxation processes described by the SSH theory simulations.

The bi-level model predictions are compared to the full simulation results in Fig. 4. Two cases are shown. The first case neglects the anharmonicity correction ($\beta = 0$) and uses values of the vibrational relaxation time τ, which are calculated by the Millikan and White correlation[4]. This case almost exactly reproduces the initial rate of production of upper level molecules. But as the simulation proceeds this combination of parameters predicts upper level populations which significantly exceed the full simulation magnitude. In the second case a value of $\beta = 5.0$ is used and the relaxation time is increased by a factor of 25. This combination of parameters is seen to overpredict the upper level populations at the beginning and end of the simulated time and underpredict the magnitude in the middle. But, the predicted upper level population is always within an order of magnitude of the full simulation value. This means that dissociation rates should also be within an order of magnitude or less of the full simulation values. For comparison, results obtained by the TT_v model are also plotted in Fig. 4. The TT_v model significantly underpredicts the initial rate of production of upper level molecules and then overpredicts this value. Increasing the value of τ used in this calculation would increase the discrepancy at the earlier simulation times but possibly improve the prediction at later times.

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In Fig. 5 the temporal evolution of atoms is plotted. The results shown are generally consistent with those of Fig. 4. The bi-level model does a very good job of predicting the vibrational energy relaxation but begins production of atoms too quickly. This discrepancy is decreased somewhat by increasing the values of τ and β. The TT_v model predicts an even higher rate of dissociation.

Further analysis and comparisons are made in the enclosed technical paper and Ph.D. dissertation. Also included in this work, are the results of axisymmetric simulations using the new bi-level model. It is seen that generally the vibrational relaxation and dissociation are slowed down using the new model. Thus, the degree of reaction and vibrational excitation tend to be reduced.

Status of the Bi-Level Model

The new bi-level model requires further testing to establish confidence in its capacity to simulate nonequilibrium flows where vibration-dissociation coupling is important. The new model shows physically reasonable trends in the compressing flows that have been tested. It is now necessary to continue this work and investigate expanding flows where the recombination process is important. An investigation of this process is underway, and a paper is in preparation for the Summer 1993 AIAA Thermophysics Conference. This new work should establish a greater basis for confidence in the new model.

Summary of Research Accomplishments

Thus, in summary, a new model for the vibration-dissociation coupling process has been developed and tested in compressing flows. This model, which incorporates more physically realistic approach shows promise for a wide range of applications. The model was based on the initial research done under this consortium agreement, which involved the detailed simulation of vibrationally relaxing and dissociating flows. Further work is underway to investigate how the new model works in expanding flows to determine how the recombination process affects the distribution of high-lying vibrational states. This work will lead to greater confidence in the new model.

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References

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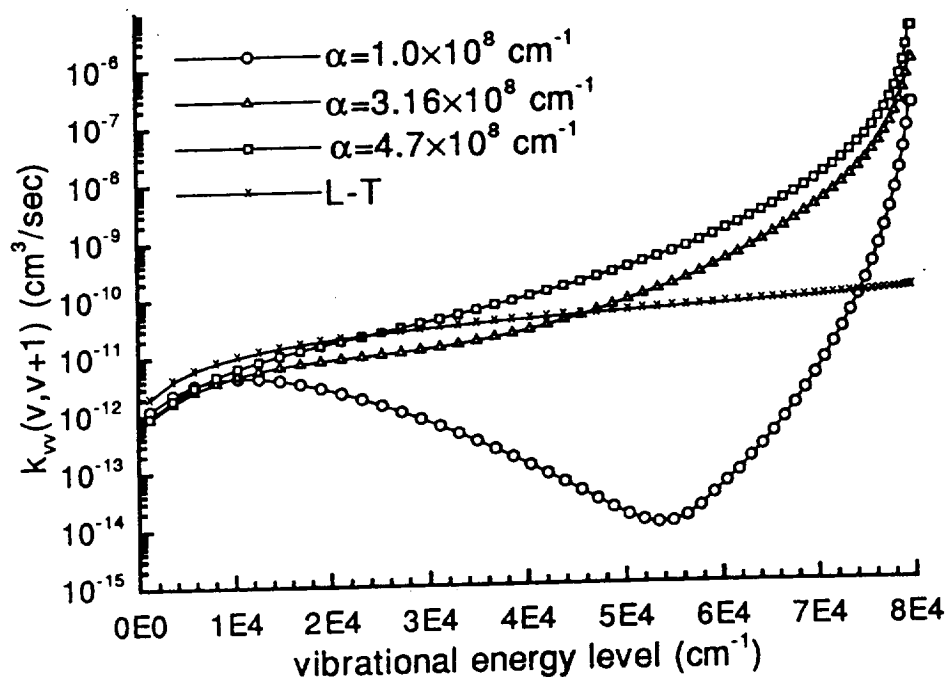
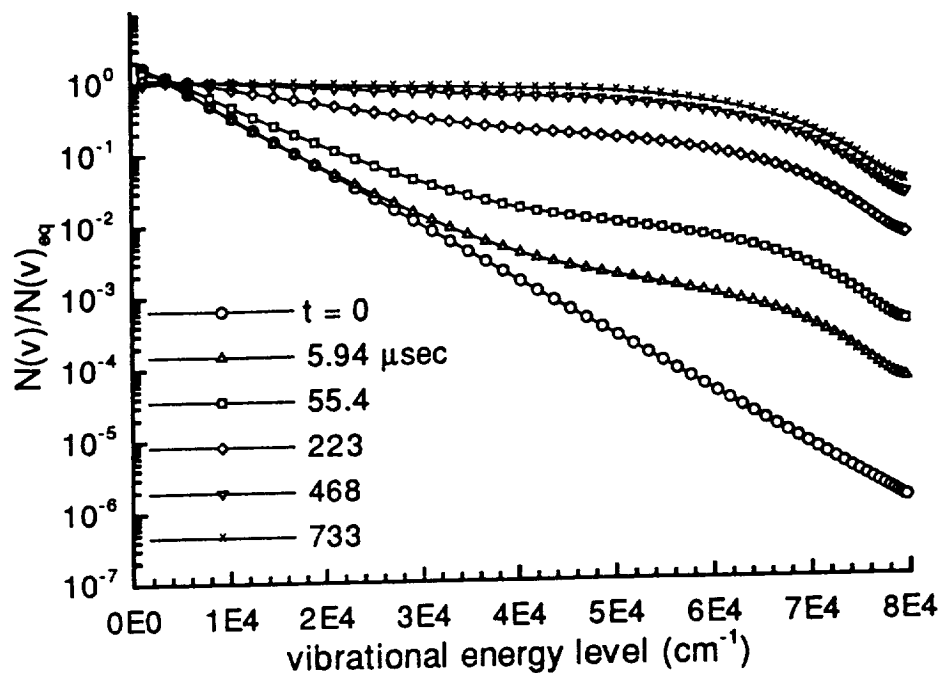**Figure 1.** Vibrational excitation rates due to collisions with N_2 molecules as calculated by SSH theory.

Figure 2. Relaxation of the normalized vibrational populations. Heating case, $\alpha = 3.16 \times 10^8 \, \mathrm{cm}^{-1}$.
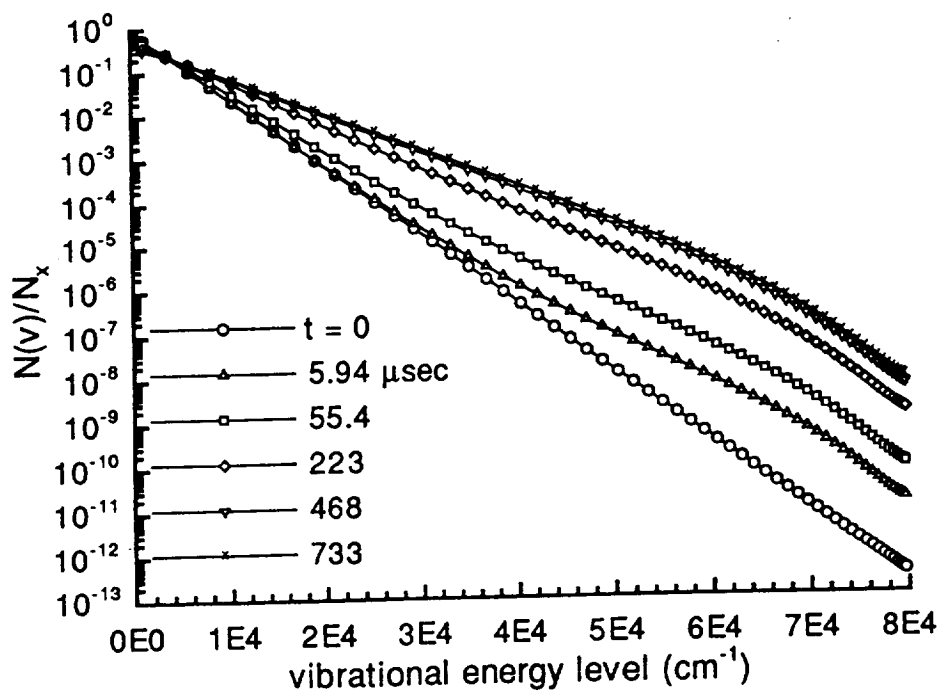

Figure 3. Number density of each vibrational level normalized by total number of molecules. Heating case, $\alpha = 3.16 \times 10^8 \, \mathrm{cm}^{-1}$.
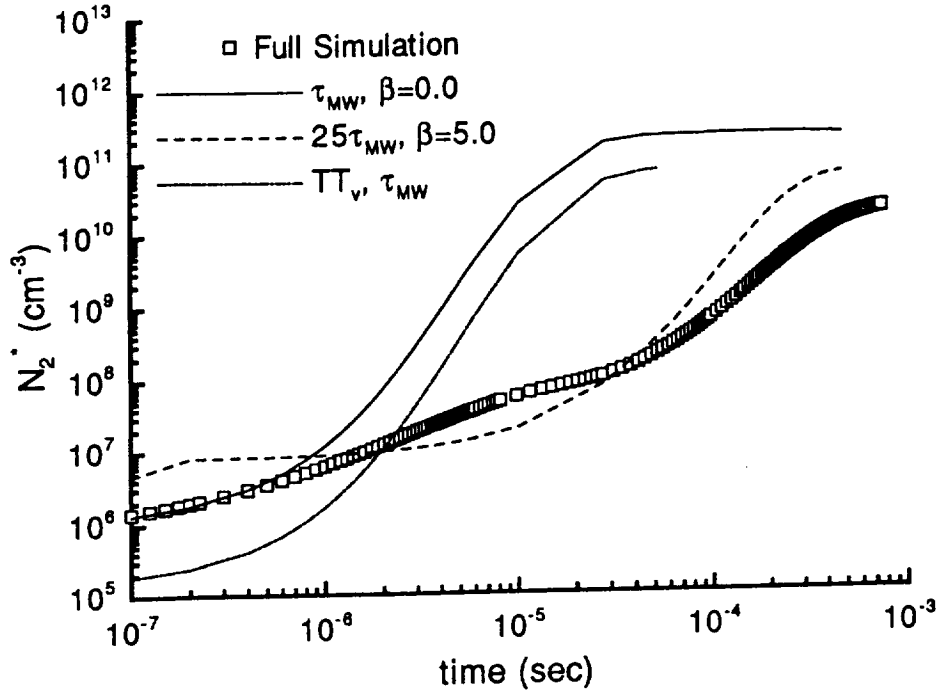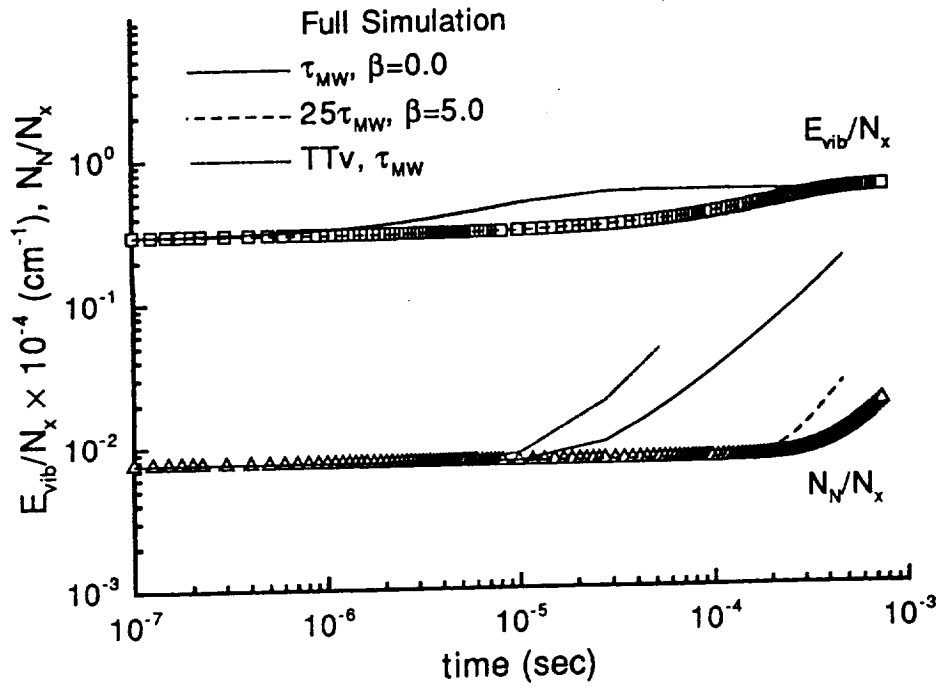
Figure 4. Relaxation of upper vibrational level populations.

Figure 5. Relaxation of the number of nitrogen atoms.