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Vibrational Relaxation and Dissociation Behind Shock Waves Part 2: Master Equation Modeling

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This paper addresses the application of the analytical nonperturbative semiclassical vibration-translation and vibration-vibration-translation forced harmonic oscillator rate models for kinetic modeling calculations. Master equation modeling of nonequilibrium dissociating gas flows, based on the forced harmonic oscillator multiple-jump rate model, is applied for simulation of vibrational relaxation and dissociation of N_2 and O_2-Ar mixtures behind strong shock waves. The comparison with the first-order rate model (Schwartz, Slawsky, and Herzfeld [SSH] theory) shows that the SSH and forced harmonic oscillator theories predict strongly different vibrational distribution functions only for times less than or equal to the vibrational relaxation time τ_{VT}. Consequently, replacing SSH rates by the forced harmonic oscillator rate model has very little effect on the calculated dissociation rate, since the dissociation incubation time is $\tau_{inc} \sim \tau_{VT}$. The incubation time calculated using impulsive and forced harmonic oscillator dissociation models also agrees well with experimental data. Thus, it is shown that vibrational relaxation, as well as nonequilibrium dissociation at hypersonic temperatures, may be satisfactorily described using the first-order, SSH vibration-vibration-translation rate model, despite the fact that this temperature region is normally clearly beyond the applicability of the SSH theory.

I. Introduction

In our previous article,[1] we discussed the validation of the semiclassical nonperturbative analytical models for the transition probabilities of vibration-translation (V-T) processes,

$$AB(i) + M \leftrightarrows AB(f) + M \tag{1}$$

and vibration-vibration-translation (V-V-T) processes,

$$AB(i_1) + CD(i_2) \leftrightarrows AB(f_1) + CD(f_2) \tag{2}$$

In Eqs. (1) and (2) AB and CD represent diatomic molecules, M stands for an atom, and i_1, i_2, f_1, and f_2 are vibrational quantum numbers. These rate models, called the forced harmonic oscillator (FHO) models, were first developed by Kerner[2] and Treanor[3] for collinear atom-diatom collisions, and by Zelechow et al.[4] for collinear diatom-diatom collisions. A comparison of the FHO models with purely quantum one-dimensional calculations, performed in the 1970s and early 1980s, showed very good agreement at low-vibrational quantum numbers and high-collision energies (see Refs. 5–10). We have also shown[1] that the FHO theory, with several simple corrections, such as symmetrization, inclusion of effects of anharmonicity, and noncollinearity of collisions, agrees remarkably well with the three-dimensional close-coupled semiclassical calculations for nitrogen by Billing and Fisher,[11] which are considered to be the most comprehensive and reliable nitrogen data available at this time. Very good agreement between the two models is shown for both the temperature and quantum number dependence of single-quantum and double-quantum vibration-vibration-translation (V-V-T) transitions in the temperature range $200 \leq T \leq 8000$ K and for vibrational quantum number $0 \leq v \leq 40$. At the same time, it is known[12,13] that first-order perturbation theory (Schwartz, Slawsky, and Herzfeld [SSH] theory) fails to predict correctly the single-quantum transition probabilities at high temperatures and high quantum numbers, and the probabilities of the multiquantum transitions. The agreement shown, as well as the simplicity of the FHO rate model, makes it attractive for master equation simulation of high-temperature nonequilibrium gas flows.

Section II of this paper presents master equation modeling, based on the FHO rates, of vibrational relaxation of gases behind a plane shock wave. The influence of multiple quantum jumps, of relaxation by collisions between excited molecules (V-V-T processes), and of nonequilibrium dissociation on the relaxation time and vibrational distribution function (VDF) is discussed. Also, the influence of the rate model (FHO or SSH) on the results of calculations is studied. Section III presents conclusions and makes recommendations on rate model applications.

II. Master Equation Calculations

In this section, we use the FHO V-V-T rate model validated in the previous paper[1] to simulate the vibrational relaxation of diatomic gases behind shock waves. Translational and rotational relaxation is not considered in the present paper (it will be shown that the relaxation times for these modes are much less than the time for vibrational relaxation, τ_{tr}, $\tau_{rot} \ll \tau_{vib}$, in the temperature range considered). The usual initial conditions for the translational temperature, pressure, density, and Mach number immediately behind the shock are given by the Rankine–Hugoniot relations, whereas the initial vibrational temperature is assumed to be equal to the gas temperature

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before the shock. State-resolved vibrational kinetics are simulated by the master equation

$$\frac{\mathrm{d}f_m}{\mathrm{d}t} = \sum_i [k_{\mathrm{at}}(i \to m) f_i - k_{\mathrm{at}}(m \to i) f_m] \cdot \frac{x_{\mathrm{at}}}{\mu_{\mathrm{at}}}\rho$$

$$+ \sum_{i,j,n} [k_{\mathrm{mol}}(i, j \to m, n) f_i f_j - k_{\mathrm{mol}}(m, n \to i, j) f_m f_n]$$

$$\times \frac{x_{\mathrm{mol}}}{\mu_{\mathrm{mol}}}\rho - f_m \frac{1}{x_{\mathrm{mol}}} \frac{\mathrm{d}x_{\mathrm{mol}}}{\mathrm{d}t}$$

$$- \left[k_{\mathrm{at}}(m \to) f_m - \rho k_{\mathrm{at}}(\to m) \left[\frac{x_{\mathrm{at}}}{\mu_{\mathrm{at}}}\right]^2 \frac{\mu_{\mathrm{mol}}}{x_{\mathrm{mol}}} \right] \cdot \frac{x_{\mathrm{at}}}{\mu_{\mathrm{at}}}\rho$$

$$- \left[k_{\mathrm{mol}}(m \to) f_m - \rho k_{\mathrm{mol}}(\to m) \left[\frac{x_{\mathrm{at}}}{\mu_{\mathrm{at}}}\right]^2 \frac{\mu_{\mathrm{mol}}}{x_{\mathrm{mol}}} \right] \cdot \frac{x_{\mathrm{mol}}}{\mu_{\mathrm{mol}}}\rho$$

$$0 \le i, j, m, n \le v_{\mathrm{diss}}, \qquad i \ne m \tag{3}$$

In Eq. (3), f_m is the relative population of the mth vibrational level of a diatomic molecule (f_m is called, hereafter, the VDF); $k_{\mathrm{at}}(i \to m)$ and $k_{\mathrm{mol}}(i, j \to m, n)$ are V-T and V-V-T rates in m^3/kmol/s, respectively; $k_{\mathrm{at}}(m \to)$ and $k_{\mathrm{at}}(\to m)$, $k_{\mathrm{mol}}(m \to)$ and $k_{\mathrm{mol}}(\to m)$ are detailed rates of dissociation (in m^3/kilomole/second) and recombination (in m^6/kilomole^2/second) on atoms and on molecules, respectively; ρ is the gas density; $x_{\mathrm{at}} = \rho_{\mathrm{at}}/\rho$ and $x_{\mathrm{mol}} = \rho_{\mathrm{mol}}/\rho$ are the mass fraction of atoms and molecules; μ_{at} and μ_{mol} are molecular masses of atoms and molecules, and v_{diss} is the vibrational level corresponding to the dissociation energy of the molecule. The V-T and V-V-T rates used in Eq. (3) are obtained by numerical averaging of the probabilities of Eq. (3) and of Eq. (4), Ref. 1, respectively, over the Boltzmann distribution. The last two terms in Eq. (3) simulate the vibration-dissociation coupling. The concentration of atoms is given by the equation

$$\frac{\mathrm{d}x_{\mathrm{at}}}{\mathrm{d}t} = 2\mu_{\mathrm{at}} \cdot \sum_1 \left[k_{\mathrm{at}}(1 \to) f_1 \frac{x_{\mathrm{mol}}}{\mu_{\mathrm{mol}}} - \rho \sum_1 k_{\mathrm{at}}(\to 1) \right.$$

$$\left. \times \left(\frac{x_{\mathrm{at}}}{\mu_{\mathrm{at}}}\right)^2 \right] \cdot \frac{x_{\mathrm{at}}}{\mu_{\mathrm{at}}}\rho + 2\mu_{\mathrm{at}} \cdot \sum_1 \left[k_{\mathrm{mol}}(1 \to) f_1 \frac{x_{\mathrm{mol}}}{\mu_{\mathrm{mol}}} \right.$$

$$\left. - \rho \sum_1 k_{\mathrm{mol}}(\to 1) \left(\frac{x_{\mathrm{at}}}{\mu_{\mathrm{at}}}\right)^2 \right] \cdot \frac{x_{\mathrm{mol}}}{\mu_{\mathrm{mol}}}\rho \tag{4}$$

The V-T and V-V-T rates in Eq. (4) are calculated using Eqs. (3) and (4) on Ref. 1. The detailed dissociation rates for atom-molecule and molecule-molecule collisions are obtained either from FHO model [see Eq. (16) of Ref. 1] or calculated using the impulsive model by Macheret and Rich[15] and normalized on the equilibrium dissociation rate constant $k_d^{\mathrm{eq}}(T)$. The recombination rates are obtained from detailed balance

$$k(\to 1) = k(1 \to) \cdot f_1(T)/K_c(T) \tag{5}$$

where $f_1(T)$ is the equilibrium vibrational distribution function, and $K_c(T)$ is the equilibrium constant.

The one-dimensional energy and motion equations of the nonequilibrium reacting gas flow behind the shock are taken from Ref. 16.

To study separately the effects of simultaneous vibrational transitions in both colliding partners and the vibrational relaxation of the excited molecules (V-V-T processes), we now consider two specific cases: 1) nearly isothermal relaxation of a diatomic gas strongly diluted by an inert diluent (O_2–Ar); and 2) relaxation of a pure gas (N_2) behind shock waves. Both cases 1 and 2 are considered in the temperature region 3–50 kK. The exponential potential parameter α in the FHO model was chosen by adjusting the calculated relaxation time

$$\tau_{\mathrm{VT}}(t) = [E_{\mathrm{vib}}(T) - E_{\mathrm{vib}}(t)]/[\mathrm{d}E_{\mathrm{vib}}(t)/\mathrm{d}t] \tag{6}$$

to available experimental data,[17–23] giving $\alpha = 3.85$ Å^{-1} for O_2–Ar and $\alpha = 4.0$ Å^{-1} for N_2 at $T \le 10$ kK. In Eq. (6), $E_{\mathrm{vib}}(T)$ and $E_{\mathrm{vib}}(t)$ are vibrational energies

$$E_{\mathrm{vib}} = \sum E_v f_v = \sum \omega_e v \cdot [1 - x_e(v+1)] \cdot f_v \tag{7}$$

where f_v can be either the equilibrium or a nonequilibrium distribution function.

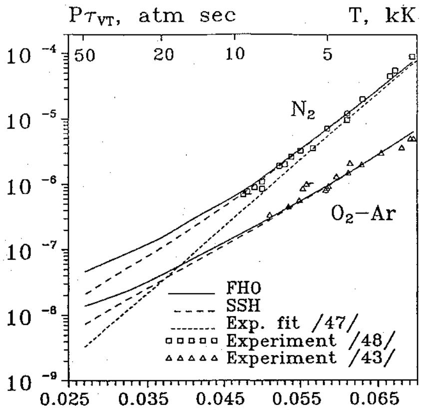

Fig. 1 Calculated V-T relaxation time for pure N_2, $\alpha = 4.0$ Å^{-1} and O_2–Ar mixture, $\alpha = 3.85$ Å^{-1}.

Figure 1 presents comparisons of the vibrational relaxation time τ_{VT} calculated using the FHO and SSH theories and also presents results of experimental measurements. The theoretical times are calculated for the conditions immediately behind the shock, i.e., for $T_v/T \ll 1$. It can be seen that the FHO and SSH theories are in very close agreement up to temperatures of $T \sim 50$ kK, where they differ by only about a factor of 2. At the lower temperatures, τ_{VT} closely agrees with the experimental fits by Millikan and White.[22] Experimental points in Fig. 1 are measurements by Appleton[23] and by Generalov and Losev.[18] It is obvious from Fig. 1 that both the experimental and the calculated τ_{VT} deviate from the Millikan–White data at the high temperatures. Formal extrapolation of the Millikan–White fit up to hypersonic temperatures leads to a considerable underestimation of the vibrational relaxation time, and at very high temperatures ($T \ge 50$ kK for nitrogen), τ_{VT} becomes less than the gas-kinetic time, $\tau_0 \sim 2 \cdot 10^{-9}$ atm·s. However, τ_{VT} given by the FHO theory exceeds τ_0 by more than an order of magnitude even at $T \sim 50$ kK (N_2) and $T \sim 30$ kK (O_2), which justifies the decoupling of vibrational and translational-rotational relaxation. The good agreement shown between the FHO and SSH theories results from the fact that the average energy transmitted to the initially unexcited harmonic oscillator in a collision is the same in FHO and SSH theories, both for atom-diatom and diatom-diatom collisions

$$\langle \Delta E(0) \rangle_{\mathrm{VT}} = \sum_{n=1} \omega n P_{\mathrm{FHO}}(0 \to n) = \sum_{n=1} \omega n \frac{\varepsilon^n}{n!} \exp(-\varepsilon)$$

$$= \omega\varepsilon = \omega P_{\mathrm{SSH}}(0 \to 1) \tag{8}$$

$$\langle \Delta E(0) \rangle_{\mathrm{VVT}} = \frac{1}{2} \sum_{n+m=1} \omega(n+m) P_{\mathrm{FHO}}(0, 0 \to n, m, \varepsilon)$$

$$= \frac{1}{2} \sum_{n+m=1} \omega(n+m) \left| C_{1,m+1}^{(n+m)} \right|^2 P_{\mathrm{FHO}}(0, n+m, 2\varepsilon)$$

$$= \frac{1}{2} \sum_{q=1} \omega q P_{\mathrm{FHO}}(0, q, 2\varepsilon) = \omega\varepsilon = \omega P_{\mathrm{SSH}}(0 \to 1) \tag{9}$$

In Eq. (9), we used the fact that

$$\sum_{k=0}^{n+m+1} \left| C_{1,k+1}^{(n+m)} \right|^2 = 1$$

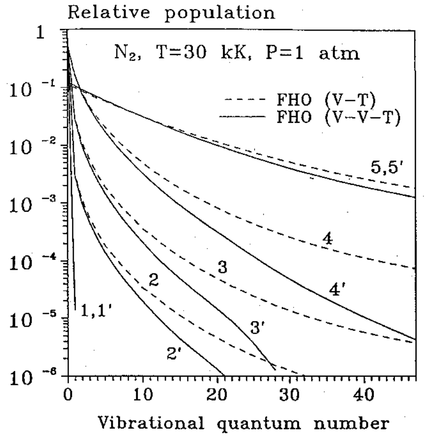

Fig. 2 Calculated time-dependent VDF of nitrogen at the constant temperature $T = 30$ kK, without dissociation: solid lines, V-V-T rate model, and dashed lines, V-T rate model; 1, 1′, $t = 0$; 2, 2′, $t = 0.1$ ns, 3, 3′, $t = 1$ ns; 4, 4′, $t = 10$ ns; 5, 5′, $t = 100$ ns; $\tau_{\mathrm{VT}} = 80$ ns.

(see Ref. 4). Equations (8) and (9) are not exact due to effects of anharmonicity and symmetrization, but the influence of these factors on the energy relaxation rate is not very strong.

Although the vibrational relaxation time for nitrogen at $T_v/T \ll 1$, plotted in Fig. 1, is calculated using part of the complete V-V-T rate matrix $k(0, 0 \to m, n)$, the solution of the master equation with this rate model requires enormous computer resources. We note that even at temperatures $T \sim 10$ kK the V-V-T processes transmitting $\Delta v_{\max} \sim 10$ quanta strongly influence the VDF at the high levels. At $T \sim 50$ kK $\Delta v_{\max}$ increases to 40–50. Thus, during master equation modeling one has to calculate $\sim 10^7$ V-V-T rates at each temperature, which takes ~100 h of VAX or ~3 h of CRAY Y/MP-8 [the complete V-T matrix $k(i \to j)$ is calculated about 60,000 times faster]. Several calculations, each for the V-T [Eq. (3), Ref. 1] and V-V-T [Eq. (4), Ref. 1] matrices, were made for nitrogen at constant temperatures, $T = 3$ kK ($\Delta v_{\max} = 5$), 10 kK ($\Delta v_{\max} = 15$), and 30 kK ($\Delta v_{\max} = 40$). It has been found that the relaxation time τ_{VT} given by both rate models is about the same. On the other hand, the VDF given by the V-V-T rate model has substantially lower values at the high v than the VDF calculated with the V-T matrix, for all considered temperatures. For example, Fig. 2 shows the time-dependent N$_2$ VDF for each of the rate models at $T = 30$ kK. We note that the VDFs calculated by SSH (V-T only) and SSH (V-T and V-V) rate models are almost identical at $T \geq 10$ kK, since SSH theory does not account for the abrupt increase in the V-V probabilities at the high-collision velocities (see the discussion in Ref. 1).

The strong effect of the V-V-T processes on the VDF may be illustrated in terms of diffusion theory of vibrational relaxation, e.g., see Refs. 24 and 25. At high temperatures, when $kT \gg \omega$, the master equation (3) may be replaced by the Fokker–Plank diffusion type equation,

$$\frac{\partial f(v,t)}{\partial t} = \frac{\partial}{\partial v}\left\{\frac{1}{2}\langle \Delta E(v,t)^2 \rangle \left(\frac{\partial f}{\partial v} - f\frac{\partial \ln f_{\mathrm{eq}}}{\partial v}\right)\right\} \tag{10}$$

where v now is a continuous variable, f_{eq} is the equilibrium VDF, and $\langle \Delta E(v,t)^2 \rangle$ is a diffusion coefficient, which represents the average square of vibrational energy transmitted in a collision

$$\langle \Delta E(v)^2 \rangle_{\mathrm{VT}} = \sum_{w} (E_v - E_w)^2 k(v \to w) \tag{11}$$

for V-T processes, and

$$\langle \Delta E(v,t)^2 \rangle_{\mathrm{VVT}} = \frac{1}{2} \sum_{v',w,w'} (E_v + E_{v'} - E_w - E_{w'})^2$$

$$\times k(v, v' \to w, w') f_v \tag{12}$$

for V-V-T processes. These functions determine the time-dependent VDF during the relaxation process. Our calculations show that $\langle \Delta E(v)^2 \rangle_{\mathrm{VVT}}$ is substantially lower than $\langle \Delta E(v)^2 \rangle_{\mathrm{VT}}$ at the high levels (see Fig. 3), which explains why the two models give such different results. Qualitatively this means that highly vibrationally excited molecules relax slower on other molecules than on structureless pseudoatoms of the same mass.

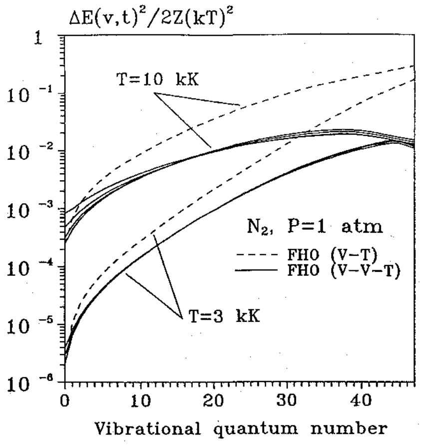

Fig. 3 Calculated average square of transmitted energy in pure nitrogen (normalized) at $T = 3$ and 10 kK; see legend to Fig. 2. Z is gas-kinetic frequency.

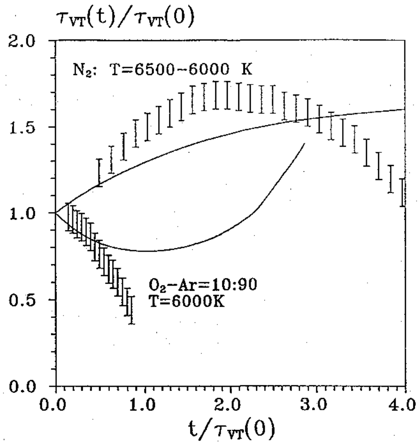

Fig. 4 Normalized time-dependent vibrational relaxation time for N$_2$ and O$_2$–Ar mixture: lines, this work; bars, experiment of Ref. 26.

From Fig. 2 one can see that the well-pronounced difference between the two N$_2$ VDFs exists only at $t \leq \tau_{\mathrm{VT}}$, whereas at $t \sim \tau_{\mathrm{VT}} \sim 10^{-7}$ atm·s the two models give very close results. Later we will show that even the huge difference between the VDFs at $t \leq \tau_{\mathrm{VT}}$, given by different rate models, has almost no effect on the dissociation. Therefore, all subsequent calculations using the FHO model presented in this paper are made for the V-T matrix.

Figure 4 shows the variation of the relaxation time for relatively strong shocks in pure N$_2$ and in an O$_2$–Ar mixture. (Calculations using SSH rate model give results very close to those of the FHO model at this temperature and, therefore, are not shown in Fig. 4.) The calculated τ_{VT} does not remain constant during vibrational excitation, even at the nearly constant temperature which can be maintained in diatom/inert diluent mixtures (for example, see Fig. 4, the O$_2$–Ar curve for which the almost constant translational temperature $T = 6000$ K is maintained). First, τ_{VT} slightly decreases due to the faster than linear increase of $\langle \Delta E(v)^2 \rangle$ with vibrational quantum number. Note that $\tau_{\mathrm{VT}}(t)$ given by Eq. (6) remains constant only if $\langle \Delta E(v)^2 \rangle \sim v$, which is only true for harmonic oscillator with single-quantum jumps.[25] Next, τ_{VT} rises sharply due to vibrational energy removal in dissociation. The calculated τ_{VT} (O$_2$–Ar) does not decrease by more than 40% during the relaxation process in the temperature range 3 kK $\leq T \leq$ 50 kK. In pure nitrogen, τ_{VT} rises as the gas cools from 6500 K to 6000 K during relaxation. The dissociation effect is not significant at these temperatures due to the long dissociation incubation period. Note that the experimental data of

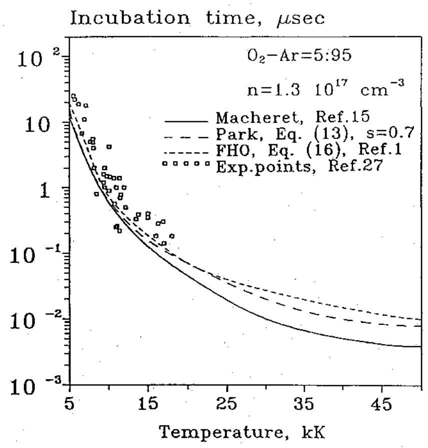

Fig. 5 Dissociation incubation time in O_2–Ar mixture: points are experimental data of Ref. 27.

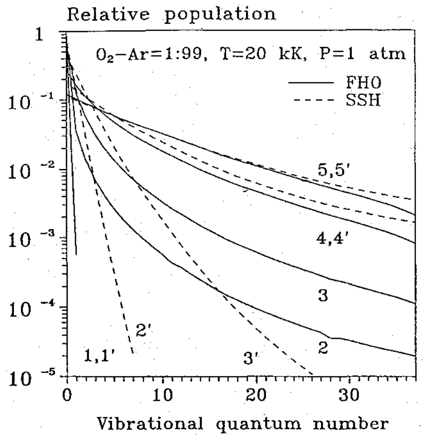

Fig. 6 Time-dependent VDF of O_2 in O_2–Ar mixture behind the shock wave: solid lines, FHO theory; dashed lines, SSH theory; 1, 1′, t = 0; 2, 2′, t = 1 ns, 3, 3′, t = 5 ns; 4, 4′, t = 25 ns; 5, 5′, t = 100 ns; τ_{VT} = 40 ns.

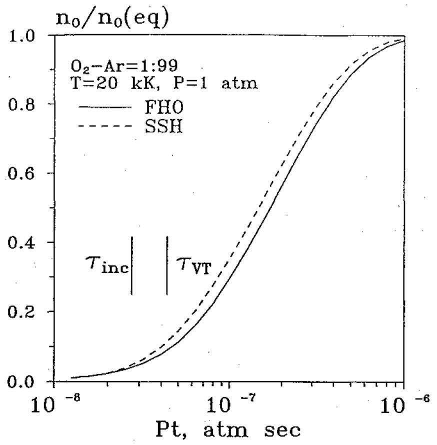

Fig. 7 Normalized time-dependent concentration of O atoms for the conditions of Fig. 6.

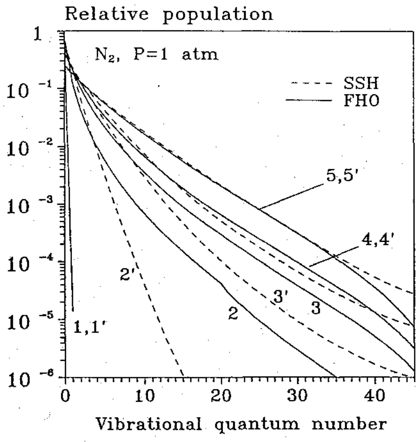

Fig. 8 Nitrogen VDF behind the shock wave: T_1 = 300 K, P_1 = 1.9 torr, U_1 = 6.5 km/s, M_1 = 18.4, T_2 = 20 kK, P_2 = 1 atm, U_2 = 1.10 km/s, M_2 = 0.38; solid lines, FHO theory; dashed lines, SSH theory; 1, 1′, z = 0; 2, 2′, z = 0.01 mm; 3, 3′, z = 0.03 mm; 4, 4′, z = 0.05 mm; 5, 5′, z = 0.12 mm.

Ref. 26 (bars in Fig. 4) reveal a somewhat steeper decrease of τ_{VT} (O_2–Ar) with time and even absolute decrease of $\tau_{VT}(N_2)$, despite the temperature drop, not accounted for by the two rate models. Similar results for pure nitrogen, also at variance with the rate models used, were also repeatedly obtained by Appleton[23] at $T = 5500$–9000 K.

Figure 5 shows the comparison of the calculated dissociation incubation time τ_{inc} defined as in Refs. 27 and 28, with the experimental data of Wray.[27] Incubation time was calculated for the O_2–Ar $= 5:95$ mixture at $N = 1.3 \cdot 10^{17}$ cm $^{-3}$, for the three dissociation models of Macheret and Rich[15] and Park[29]:

$$k_d(T, T_v) = k_d^{\mathrm{eq}}\left(T^s, T_v^{1-s}\right), \quad s = 0.7 \qquad (13)$$

and by the FHO model [see Eq. (16), Ref. 1]. One can see that all three models agree well with the experimental data and each other. (The FHO dissociation model also gives very close agreement with a revised impulsive model by Macheret et al.[14]; this has not been shown in Fig. 5.) The reason for such a weak dependence of the incubation time on the dissociation model is that τ_{inc} is approximately equal to the time for the V-T relaxation to some quasi-steady-state vibrational temperature $T_v^* \leq T$, controlled by the rate of vibrational energy removal into dissociation. T_v^* is weakly dependent on the dissociation model and, therefore, one should expect the ratio $\tau_{\mathrm{inc}}/\tau_{VT}$ to be of the order of unity, slightly decreasing with temperature. This fact makes the incubation time an insufficient criterion for the validation of dissociation models, and further studies in this direction are needed.

Figures 6 and 7 show the time-dependent vibrational distribution function of O_2 and the atom concentration behind the shock, calculated by FHO and SSH theories, respectively, and using the revised Macheret model for dissociation. The incident gas flow parameters are the following: $T_1 = 300$ K, $P_1 = 2.9$ torr, $U_1 = 4.65$ km/s, $M_1 = 14.4$, which gives the temperature behind the shock $T_2 = 20$ kK, at nearly atmospheric pressure, and $U_2 = 1.05$ km/s, $M_2 = 0.39$, One may see that, again, considerable difference between the VDFs calculated by the FHO and SSH models exists only at $t \leq \tau_{VT}$ (see Fig. 6), when the dissociation is still inhibited (see Fig. 7). The dissociation begins only at $t \geq \tau_{\mathrm{inc}} \sim \tau_{VT}$, when the two models already give very close results of the VDF (see Fig. 7). Thus, the incubation time and the dissociation rate become essentially unaffected by the V-V-T rate model used in the calculation (see Fig. 7). Similar results were obtained over the entire temperature range $5 \leq T \leq 50$ kK. This is expected, since at these temperatures the ratio $\tau_{\mathrm{inc}}/\tau_{VT}$ is close to unity, $1.5 \geq \tau_{\mathrm{inc}}/\tau_{VT} \geq 0.5$, decreasing toward the high temperatures, which agrees well with the Wray data.[27] Note that at the higher temperatures the VDF never reaches vibrational equilibrium at $T = T_v$, due to intensive energy removal into dissociation, which continues until the complete dissociation of the molecular fraction.

Very similar results, shown in Figs. 8 and 9, have been obtained for pure nitrogen for the following conditions: $T_1 = 300$ K, $P_1 = 1.9$ torr, $U_1 = 6.5$ km/s, $M_1 = 18.4$, which give $T_2 = 20$ kK, $P_2 = 1$ atm, $U_2 = 1.10$ km/s, $M_2 = 0.38$ immediately behind the shock. In these calculations, the temperature behind the shock decreases during the vibrational relaxation and dissociation from 20 to about 7 kK at equilibrium; both FHO and SSH theories give very similar dependence of temperature on time (see Fig. 9). In Fig. 9, T_v is the vibrational temperature of N_2,

$$T_v = \frac{\omega_e(1 - 2x_e)}{\ln[f_0/f_1]} \qquad (14)$$

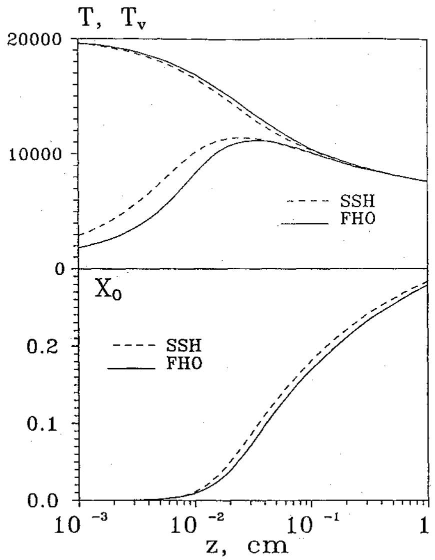

Fig. 9 Temperature, vibrational temperature and mass fraction of *N* atoms behind the shock for the conditions of Fig. 8.

We conclude from these calculations that first-order perturbation (SSH) theory may be used for simulation of nonequilibrium hypersonic flows in pure and diluted gases behind strong shock waves with reasonable accuracy. Despite the incorrect prediction of the VDF on the early stage of relaxation, SSH theory, combined with the experimentally validated dissociation model, can provide reliable dissociation rates. In a mixture of gases with differing V-T relaxation times, such as an N_2–O_2 mixture (the difference between $\tau_{VT}(N_2)$ and $\tau_{VT}(O_2)$ can be seen in Fig. 1), the situation becomes more complicated. The oxygen dissociation starts much earlier than that of nitrogen, and it occurs at characteristic times $\tau_{inc}(O_2) \sim \tau_{VT}(O_2) \leq t \leq \tau_{inc}(N_2) \sim \tau_{VT}(O_2)$, when the N_2 VDF is underpredicted by SSH theory at high vibrational levels. However, this will be unlikely to lead to any significant underestimate of NO production in the vibrationally stimulated Zel'dovich mechanism reactions

$$\begin{aligned} N_2(v) + O &\rightarrow NO(v') + N \\ O_2(v) + N &\rightarrow NO(v') + O \end{aligned} \qquad (15)$$

This is because the rate-determining reaction $N_2(v) + O \rightarrow NO + N$ has a relatively low-energy threshold corresponding to $v \sim 12$, where the VDF given by SSH theory reasonably agrees with the FHO model, even at $t \leq \tau_{VT}$.

III. Summary

Master equation modeling of nonequilibrium dissociating gas flows, based on the FHO rate theory, has been applied for simulation of vibrational relaxation and dissociation of N_2 and O_2–Ar mixture behind strong shock waves. It is shown that the V-T relaxation time τ_{VT} given by the SSH theory is in fairly good agreement with the FHO theory in the temperature range $T = 3$–50 kK. The VDF calculated by the SSH theory has much lower populations at the high vibrational levels than predicted by the FHO theory, at $t \leq \tau_{VT}$, due to the effect of multiple jumps. Similarly, the VDF calculated using the complete V-V-T matrix rate model has lower values than the distribution function given by the V-T FHO matrix. However, it is shown that the effect of the V-T rate model on the calculated dissociation incubation time τ_{inc} and on the dissociation rate is weak, since SSH, FHO (V–T), and FHO (V-V-T) models agree well at $t \geq \tau_{VT}$, whereas $\tau_{inc}/\tau_{VT} \sim 1$ for $T = 5$–50 kK. The incubation time calculated using the FHO dissociation model agrees well with experimental data by Wray[27] for O_2–Ar and with the impulsive dissociation model by Macheret and Rich.[15]

The FHO model gives new insight into vibrational relaxation kinetics at high temperatures and may be used for testing of more simplified, first-order rate models. The present results show that the first-order perturbation theory (SSH) may be satisfactorily used for simulation of vibrational relaxation of quite high temperatures, well beyond its previously assumed range of validity.

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