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Coupled Vibration-Dissociation-Exchange Reactions Model for Hypersonic Airflow Computations

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A preferential coupled vibration-dissociation and exchange reactions-vibration model resulting from an extension of the well-known Treanor and Marrone coupled vibration-dissociation-vibration model has been derived to take into account the coupling between the vibrational excitation of the N_2 and O_2 molecules and the two Zeldovich exchange reactions. Analytical expressions for the exchange reactions coupling factor and for the average vibrational energy lost—or gained—by a molecule through an exchange reaction have been developed. The influence of such a coupling has been shown by means of numerical simulations of hypersonic airflows through different configurations: normal and bow shock waves, wind-tunnel nozzle, and boundary layer. Code-to-code comparisons of our model and other recent approaches and code-to-experiments comparisons have been conducted for the one-dimensional flow behind a normal shock wave. These comparisons have shown good agreement of our model results with the experimental data.

I. Introduction

THE interaction between vibrational relaxation and chemical processes is significant in many gasdynamics environments such as high-enthalpy airflows. The domain of study of such coupling phenomena concerns a 5-species air mixture (N_2, O_2, NO, N, and O) governed by a 17-chemical reaction scheme: 15 dissociation reactions and the 2 Zeldovich exchange reactions. The molecules N_2 and O_2 are taken in vibrational nonequilibrium, whereas NO is assumed to be in vibrational equilibrium because of its small vibrational relaxation time in comparison with the characteristic flow time scale. The vibrational relaxation of N_2 and O_2 is considered to occur via the vibration-translation energy exchanges (Landau–Teller model[1]) in addition to the vibration-chemistry exchanges that are the focus of this study. The order of magnitude of the relaxation time of the vibrational process and of the chemical reactions being similar, there results a strong coupling between these nonequilibrium phenomena. Such a coupling proceeds in two different ways: the influence of the vibration on the chemical reactions and the reverse effect. Furthermore, two kinds of coupling must be investigated: the coupling between the vibration and the dissociation reactions on the one hand and the coupling between the vibration and the exchange reactions on the other hand. Just behind the shock wave, the translational temperature reaches its peak value while the vibrational temperature lags because it takes a finite time for the vibration to be excited. In this case, the taking into account of the coupling leads to a decrease in the rate of dissociation, and because the dissociation removes vibrational energy, the vibrational temperature is higher than when the dissociation does not depend on the vibrational excitation.

The influence of the vibrational excitation of the molecules on their dissociation was studied in 1959 by Hammerling et al.,[2] who proposed a model called the coupled vibration-dissociation (CVD) model. Their theory led to a modification of the classical Arrhenius description by means of a coupling factor V_D. Then, in 1962, Treanor and Marrone[3] completed this model by considering also the influence of the molecular dissociation on the average vibrational energy of the molecules [coupled vibration-dissociation-vibration (CVDV)]: the vibrational energy removed by dissociation or gained by recombination was included in the vibrational relaxation equation as an additional source term ω_{DV}. Then, in 1963, Marrone and Treanor[4] also defined a preferential character of such a coupling via a variable U_D (with the dimension of a temperature measuring the extent to which the upper vibrational levels are more reactive than the lower levels because of a cross-sectional enlargement at high excitation), leading to a more realistic model: The coupling is said to be preferential when the dissociations occur from the highest vibrational levels only and nonpreferential when the dissociations can occur from any level. In 1988, Park[5] proposed a two-temperature model to describe the vibration-dissociation coupling, built on an empirical formula fitting experimental data. More recently, in 1994, analytical rates of dissociation based on the classical impulsive approach have been presented by Macheret et al.[6] All of these previous models have been derived for dissociation reactions only and do not take into account the exchange reactions.

Whereas the coupling between the vibration and the dissociation has been studied for over three decades, the coupling between the vibrational relaxation and the exchange reactions has been the subject of recent studies only. This coupling is of practical relevance in the high-speed flow regime because the bimolecular chemical exchange reactions involving O_2, N_2, and NO molecules are of great importance in the high-temperature air kinetics. In 1996, Bose and Candler[7] proposed a new model based on theoretical investigations to derive the kinetic rate constants of the first exchange reaction under rotational and vibrational nonequilibrium. It is now certain that the level of NO molecules in the mixture is driven mainly by the coupling of the vibrational relaxation onto the first exchange reaction.[7] Empirical formulation for the nonequilibrium exchange reaction kinetic rate constant had been proposed in 1990 by Macheret et al.,[8] and in 1995 Knab et al.[9] developed a coupled vibration-chemistry-vibration (CVCV) model for the full coupling between the vibration and all of the chemical reactions (dissociation and exchange reactions), based on the Treanor and Marrone approach and on the Warnatz vibrational state specific rate constants. Similarly, Zeitoun et al.[10,11] used a nonpreferential coupling factor $V_E(T, T_V)$ for the exchange reactions, based on the vibrational state specific rate constants specially derived for the exchange reactions.

On the basis of theoretical reflections given by Knab et al.[9] on consistency to be satisfied by every coupling model, we propose in this paper a preferential formulation of our coupling factor $V_E(T, T_V)$, as well as an upgrade of our vibration-exchange reactions coupling

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source term ω_{EV} that guarantees the consistency requirement because previously it was derived from a rough extension of the Treanor and Marrone coupling source term to all the reactions. Let us first state that this upgraded model, referred to as the CVDEV model, relies on the vibrational state specific rate constants used in our former model[11] and is thus different from the CVCV model. Moreover, the coupled vibration-dissociation and exchange reactions-vibration (CVDEV) model has the advantage of including the Treanor and Marrone CVDV model in the case of dissociation reactions.

The aim of this paper is to apply the CVDEV model to the numerical computations of hypersonic airflows. In one-dimensional simulations, the results obtained with this model have been compared with other models—Treanor and Marrone CVDV,[3,4] Macheret et al. (Macheret–Fridman–Rich; MFR),[6,8] Knab CVCV,[9] Park[5] coupling applied to the first exchange reaction ($N_2 + O \rightarrow NO + N$) according to Ref. 12—and with recent shock tube experimental data giving the NO infrared radiation behind a normal shock wave.[13] The effects of the CVDEV model have also been illustrated by means of quasi-one-dimensional steady flow computations of the free piston shock tube of Marseilles (TCM2) hypersonic nozzle. Finally, two-dimensional computations around the Lobb[14] sphere by means of a recent extension of the defect boundary-layer theory to real gas effects[15] coupled to the inviscid flow are also presented.

II. CVDEV Model

A. Fundamental Relations

Extending the previous work,[2,3] one examines the influence of the vibrational excitation not only on the dissociation reactions but also on the exchange reactions. Such a complete modeling is necessary because the chemical relaxation process of nitric oxide NO is governed by this type of reaction. Let us consider the formal exchange reaction of the vibrationally excited molecule $A_2^*(v)$ with the particle B:

$$A_2^*(v) + B \not\Leftrightarrow AB + A$$

where v is the vibrational level. This reaction is a part of the overall reaction

$$A_2 + B \not\Leftrightarrow AB + A$$

and characterizes the decomposition of the molecule A_2 from the particular vibrational quantum state v. This reaction occurs if, during the collision with a nonvibrating particle B, the activation threshold is overcome. The exchange reactions indeed are characterized by an activation threshold ε_A that is less than the dissociation energy ε_D characterizing the dissociation process. Considering the limiting case $\varepsilon_A \rightarrow \varepsilon_D$ provides rate constants and transferred energy expressions for the dissociation reactions. The question then to be solved is how the vibrational excitation influences the reaction process.

Before answering this question, let us recall the expression of the production rate for a vibrational level v:

$$\dot{\omega}_{A_2(v)} = \frac{\mathrm{d}}{\mathrm{d}t}[A_2(v)] = k(v, T)[A_2(v)][B]$$

where $k(v, T)$ is the vibrational state specific rate constant and the brackets denote the number density. The overall production rate reads

$$\dot{\omega}_{A_2} = \frac{\mathrm{d}}{\mathrm{d}t}[A_2] = K_f[A_2][B]$$

with K_f the overall kinetic rate constant. Because

$$\dot{\omega}_{A_2} = \sum_{v=0}^{v\max(A_2)} \dot{\omega}_{A_2(v)}$$

where $v\max(A_2)$ denotes the maximum number of vibrational energy states of the A_2 molecules, one obtains

$$K_f = \sum_{v=0}^{v\max(A_2)} k(v, T) n_{A_2}(v)$$

with $n_{A_2}(v) = [A_2(v)]/[A_2]$ the vibrational distribution function. Let us define, as in Ref. 3, the following dimensionless coefficient

$$p_E(v) \equiv \frac{\dot{\omega}_{A_2(v)}}{\dot{\omega}_{A_2}} = n_{A_2}(v)\frac{k(v, T)}{K_f} \tag{1}$$

The subscript E refers to the exchange reaction process. The term $p_E(v)$ represents the probability of an exchange reaction occurring from the vth level. Consequently, the average vibrational energy loss in a decomposition of a molecule A_2 through an exchange reaction is

$$\overline{\varepsilon_{V_{A_2}}^{l,E}} = \sum_{v=0}^{v\max(A_2)} \varepsilon_{A_2}(v) p_E(v)$$

where $\varepsilon_{A_2}(v)$ denotes the vibrational energy content of the level v. Consequently, one obtains the following fundamental relations:

$$\overline{\varepsilon_{V_{A_2}}^{l,E}} = \sum_{v=0}^{v\max(A_2)} \varepsilon_{A_2}(v) n_{A_2}(v)\frac{k(v, T)}{K_f} \tag{2}$$

and

$$V_E = \frac{K_f}{K_f^0(T)} = \sum_{v=0}^{v\max(A_2)} \frac{k(v, T) n_{A_2}(v)}{K_f^0(T)} \tag{3}$$

where $K_f^0(T)$ is the kinetic rate constant at the vibrational equilibrium. If a distribution function $n_{A_2}(v)$ and an oscillator model giving $\varepsilon_{A_2}(v)$ have been chosen, then the coupling factor V_E and the vibrational energy removed $\overline{\varepsilon_{V_{A_2}}^{l,E}}$ depend only on the modeling of the vibrational state specific rate constant $k(v, T)$. This is in the sense that a chemistry-vibration coupling model is said to be physically coherent.[9]

B. Vibrational State Specific Rate Constant Modeling

The basis of our model is the choice adopted for the vibrational state specific rate constant $k(v, T)$. Considering the modeling from Refs. 10 and 11, one gets

$$k(v, T) = \begin{cases} C(T)A_0(T)\exp\left(-\dfrac{\varepsilon_A - \varepsilon(v)}{kT}\right) & \varepsilon(v) < \varepsilon_A \\ C(T)A_0(T) & \varepsilon(v) > \varepsilon_A \end{cases} \tag{4}$$

The term $C(T)$ must be determined, and $A_0(T)$ is given by Arrhenius:

$$K_f^0(T) = A_0(T)\exp(-\varepsilon_A/kT)$$

To introduce a preferential character in the exchange reactions, one no longer considers the modeling [Eq. (4)] but the following:

$$k'(v, T) = k(v, T) \times F(v)$$

with $F(v)$ proportional to the probability of a molecule on the vth vibrational level to disintegrate in a sufficiently energetic collision governed by an exchange reaction:

$$F(v) = \begin{cases} \exp\left(-\dfrac{\varepsilon_A - \varepsilon(v)}{kU_E}\right) & 0 \le v \le N_A - 1 \\ 1 & N_A \le v \le N_D - 1 \end{cases} \tag{5}$$

where N_A is the number of vibrational levels of the molecule corresponding to the activation energy ε_A. The expression [Eq.(5)] is similar to that of Treanor and Marrone, $F(v) = \exp\{-[\varepsilon_D - \varepsilon(v)]/kU_D\}$, $0 \le v \le N_D - 1$, but with the following particularity: If through an exchange reaction a molecule is on a vibrational level $v > N_A$, it disintegrates whatever the level $v\,(> N_A)$ is. Therefore, only the vibrational levels lower than N_A must be preferentialized, whereas for the dissociation all of the vibrational levels are preferentialized. The terms U_D and U_E describe how rapidly the chemical reaction drops off for low values of v. Hence the higher the level is, the greater its probability of reaction. Note that, when $U_D = \infty$ or $U_E = \infty$, $F(v) = 1$, which corresponds to the equal probability assumption leading to nonpreferential reaction. Thus, for the exchange reactions, the vibrational state specific rate constant modeling reads

$$k'(v, T) = \begin{cases} X(T)\exp\left(-\dfrac{\varepsilon_A}{kU_E}\right)\exp\left[\dfrac{\varepsilon(v)}{k}\left(\dfrac{1}{T} + \dfrac{1}{U_E}\right)\right] & 0 \le v \le N_A - 1 \\ X(T)\exp\left(\dfrac{\varepsilon_A}{kT}\right) & N_A \le v \le N_D - 1 \end{cases} \tag{6}$$

with $X(T) = C(T)K_f^0(T)$.

C. Exchange Reaction Coupling Factor

If the expression [Eq. (6)] for $k'(v, T)$ is inserted into the general expression of the coupling factor [Eq. (3)], under the assumption of the Boltzmann distribution characterized by the vibrational temperature T_V, one obtains by summing up over the limited number of energy levels of a cutoff harmonic oscillator the following expression:

$$V_E^{\mathrm{CVDEV}}(T, T_V, U_E) = \frac{Q_V^{N_D}(T)}{Q_V^{N_D}(T_V)} \cdot \frac{\mathrm{Up}}{\mathrm{Down}} \tag{7}$$

with

$$\mathrm{Up} = Q_V^{N_A}(T_F)\exp(-\varepsilon_A/kU_E) + Q_V^{N_D-N_A}(T_V)\exp\{(\varepsilon_A/k)[(1/T)-(1/\alpha T_V)]\}$$

and

$$\mathrm{Down} = Q_V^{N_A}(-U_E)\exp(-\varepsilon_A/kU_E) + Q_V^{N_D-N_A}(T)\exp\{(\varepsilon_A/kT)[(\alpha-1)/\alpha]\}$$

where T_F is defined as

$$1/T_F = (1/T_V) - (1/T) - (1/U_E)$$

and $\alpha = \varepsilon_A/\varepsilon_{v_A}$, where ε_{v_A} is the energy corresponding to the vibrational level in the harmonic oscillator just above the activation energy ε_A. Note that the function $C(T)$ appearing in Eq. (6) has been determined at thermal equilibrium writing $V_E(T, T_V = T, U_E) = 1$ and that

$$Q_V^m(x) = \frac{1-\exp[-(m\theta_V)/x]}{1-\exp(-\theta_V/x)}$$

has been defined for simplicity.

D. Exchange Reaction-Vibration Coupling Source Term

As first introduced by Treanor and Marrone, the influence of the dissociation recombination processes on the vibrational energy implies an additional source term of loss or gain in each vibrational relaxation equation:

$$\omega_{DV} = \left(\overline{e_V^{g,D}} - e_V^{N_D}\right)\dot{\omega}^{g,D} - \left(\overline{e_V^{l,D}} - e_V^{N_D}\right)\dot{\omega}^{l,D} \tag{8}$$

with $\dot{\omega}^{g,D}$ and $\dot{\omega}^{l,D}$ being, respectively, the rate at which a molecule is created or destroyed through the dissociation process. To take into account the exchange reaction-vibration coupling, one must introduce an additional source term in the vibrational equation that reads

$$\omega_{EV}^{\mathrm{CVDEV}} = \left(\overline{e_V^{g,E}} - e_V^{N_D}\right)\dot{\omega}^{g,E} - \left(\overline{e_V^{l,E}} - e_V^{N_D}\right)\dot{\omega}^{l,E} \tag{9}$$

with $\dot{\omega}^{g,E}$ and $\dot{\omega}^{l,E}$ being, respectively, the overall production and destruction rate of the excited molecule through the exchange reactions. The term $e_V^{l,E}$ is the vibrational energy loss through an exchange reaction and reads

$$\overline{e_V^{l,E}} = \frac{A_1^l + A_2^l}{A_3^l + A_4^l} \tag{10}$$

with

$$A_1^l = \exp[-(\varepsilon_A/kU_E)]Q_V^{N_A}(T_F)e_V^{N_A}(T_F)$$

$$A_2^l = \exp(\varepsilon_A/kT)\left\{Q_V^{N_D}(T_V)e_V^{N_D}(T_V) - Q_V^{N_A}(T_V)e_V^{N_A}(T_V)\right\}$$

$$A_3^l = \exp(-\varepsilon_A/kU_E)Q_V^{N_A}(T_F)$$

$$A_4^l = \exp\{(\varepsilon_A/k)[(1/T)-(1/\alpha T_V)]\}Q_V^{N_D-N_A}(T_V)$$

As in the Treanor and Marrone theory, the expression of the vibrational energy gain through a recombination that occurs during an exchange reaction is obtained by writing

$$\overline{e_V^{g,E}} = \lim_{T_V \to T} \overline{e_V^{l,E}}$$

It is interesting to observe that for the dissociation reaction ($\varepsilon_A \equiv \varepsilon_D$ and $U_E \equiv U_D$) the expressions of the coupling factor V_E and of the vibrational energy loss $\overline{e_V^{l,E}}$ and gain $\overline{e_V^{g,E}}$ coincide exactly with the expressions given by Treanor and Marrone, in both preferential and nonpreferential cases. Hence our coupling factor and vibrational energy loss and gain formulas are applicable for dissociation reactions as well as for exchange reactions.

E. Remark

Comparing the present model to the Knab et al.[9] CVCV model leads to the following comments. Both models are based on the Treanor and Marrone approach, and the expressions for the vibrational state specific rate constant [Eq. (6)] are different from the Warnatz ones used by Knab et al.[9] Nonetheless, both models lead to identical expressions of V_E^{CVDEV} and $\omega_{EV}^{\mathrm{CVDEV}}$ in the nonpreferential case, whereas our expressions are different in the preferential case; our approach depends only on the adjustment of a parameter U_E, whereas the Knab model depends also on the adjustment of a second parameter α that was adjusted to 0.8 to fit the Warnatz results concerning the dissociation vibration coupling. On the other hand, our model retrieves exactly the Treanor and Marrone CVDV model in the case of coupling between vibration and dissociation, whereas the Knab model needs to force $\alpha = 1$ to get the same results as Treanor and Marrone. Both models' parameters are subject to variation: Fitting them to either experimental results or to data obtained using more physically proven models,[7] one can attain the combination of simplicity and adequacy,[16] which makes their incorporation into existing high-enthalpy flow codes easier.

III. Results and Discussion

The present model is illustrated and compared with other models and with experimental data by means of numerical simulations of one-dimensional and two-dimensional hypersonic flows. In all of the computations, the backward kinetic rate constant K_b is computed as the ratio of K_f^0 to the equilibrium rate constant K_{eq} given by classical thermodynamics. Behind a steady shock wave, the thermochemically relaxing flow is described by one-dimensional steady Euler equations. These equations are solved using the standard routine LSODE,[17] an integrator of stiff ordinary differential equations. Concerning the two-dimensional inviscid flow computations, they are performed using an inviscid version of the CEVHYNE code.[18] The viscous flow is obtained with a defect boundary-layer approach coupled to the inviscid flowfield to take into account vorticity effects in the shock layer.[15]

A. Preferentialization Effects in the CVDEV Model

The influence of the preferential character of CVDEV on the nonequilibrium phenomena behind a shock wave has been shown through a Mach 11.07 test case whose conditions ($P_\infty = 300$ Pa, $U_\infty = 3850$ m/s, $X_{\mathrm{N}_{2\infty}} = 0.777$, and $X_{\mathrm{O}_{2\infty}} = 0.223$) correspond to upstream conditions used by Treanor et al.[12] The rate of reactions in thermal equilibrium is the same as in Ref. 13, where they were incorporated from Refs. 19 and 20, and the various vibrational translational relaxation times are also taken from Ref. 13. The influence of the preferential coupling on the flow parameters is tested by means of different constant values of U_D and U_E.

We have chosen to show in Figs. 1 and 2 the evolution behind the normal shock wave of the NO infrared radiation profiles computed via the formula given in Ref. 12 [following a discussion with I. V. Adamovich, the authors would like to mention the following corrections of the typographic errors appearing in Treanor et al.[12]: the y-axis titles in Figs. 3 and 4, p. 196, should be Intensity (10^4 W/cm$^3 \cdot$ sr)] and from the profiles of nitric oxide mass fraction Y_{NO} obtained by the CVDEV model with different values of U_D and U_E. In these figures, one can notice that taking into account the preferentiality only in the dissociation reactions leads to an increase and to a forward movement of the maximum of Y_{NO}. Indeed, at these temperatures, it essentially delays the O_2 dissociation; thus more O_2 molecules can react with the N atoms, leading to more NO in the mixture. In Fig. 1, the influence of the preferential coupling on the first Zeldovich reaction is shown. As and when $U_{E_{\mathrm{N}_2}}$ decreases, i.e., as and when the coupling is more and more preferential, the maximum of Y_{NO} decreases and moves back because one delays the $\mathrm{N}_2 + \mathrm{O} \rightarrow \mathrm{NO} + \mathrm{N}$ reaction. The same kind of analysis has

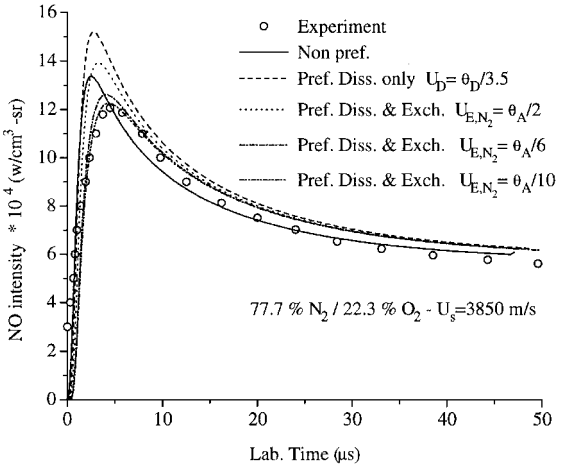


Fig. 1 NO IR radiation profiles: influence of $U_{E_{N_2}}$; P_∞ = 300 Pa.

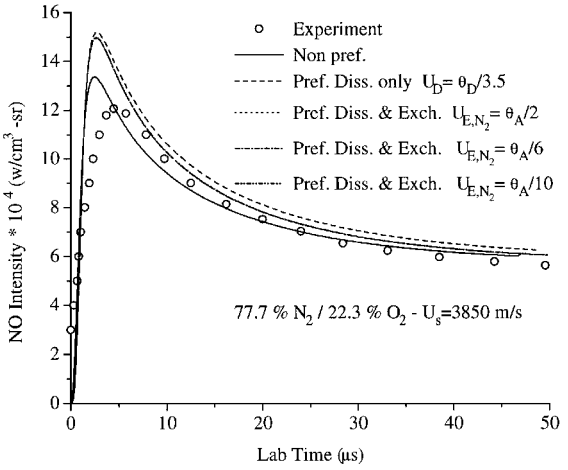


Fig. 2 NO IR radiation profiles: influence of $U_{E_{O_2}}$; P_∞ = 300 Pa.

been done for the molecule O_2 (Fig. 2). Concerning the preferentialization of the second exchange reaction, the different values of $U_{E_{O_2}}$ have no influence on Y_{NO} because the evolution of O_2 comes essentially from the reactions of dissociation. This result implies that it is unnecessary to look for an adjustment of the preferentialization parameter U_{O_2} in the exchange reaction involving O_2, which is in quite good agreement with Losev et al.[16] when they claim that it is not necessary to take into account the influence of the vibration on the kinetics of this reaction: the kinetic rate constant of this reaction can be determined with only the temperature T. To summarize the influence of the preferentializationof the coupling on the NO concentration, [NO] increases if $U_{D_{N_2}}$ or $U_{D_{O_2}}$ decreases; [NO] decreases if $U_{E_{N_2}}$ decreases.

B. Comparison Between Different Models and with Experimental Data

The CVDEV model has been applied to two sets of numerical simulations of one-dimensional flow behind a shock wave corresponding to two upstream mixtures: 77.7%N_2/ 22.3%O_2 and 60%N_2/ 40%O_2. For each mixture, four test cases with different upstream velocities have been computed (Table 1). These test cases correspond to experiments carried out by Wurster et al.,[21] and the experimental facilities are described in this reference. One can state here that these experiments consist of measuring the time history of infrared (IR) radiation behind a normal shock wave in a pressure-driven shock tube. To do that and as decribed in Ref. 21, the authors used an indium antimonide (InSb) detector in the radiometer to measure the NO IR radiation behind the shock wave. This observed in-band IR radiation is related to the NO concentration and the gas translational temperature. Figure 3 shows the NO infrared radiation intensity profiles behind the normal shock wave predicted by different models

Table 1 Shock wave experiments of Wurster et al.[21] at P_∞ = 300 Pa; values of X_D and X_E

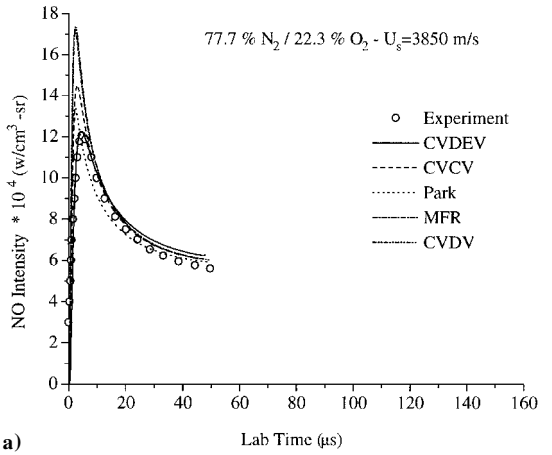
77.7%N_2/ 22.3%O_2			60%N_2/ 40%O_2		
U_∞, m/s	X_D	X_E	U_∞, m/s	X_D	X_E
3850	3.5	10	3850	6	4
3520	2	10	3470	3	4
3260	1	10	3240	1	4
2990	1	10	3060	1	4

and compared with the experimental data. The different models are those described in the Introduction. The results obtained with the CVDEV model have been computed with values of U_D and U_E that give the best agreement with the experimental data. For the present test cases, the values of U_D and U_E are θ_D/X_D and θ_A/X_E, where X_D and X_E are given in Table 1. The values of U_D are also used in the CVDV model. As for the CVCV model, the values of the parameters α and U are the same as those in Ref. 9.

First of all, for each mixture one notes that, at the high shock wave velocities ($U_\infty > 3400$ m/s), there exists the well-known overshoot in radiation intensity before the NO concentration reaches equilibrium.[13] Moreover, the lower the Mach number is, the farther the computed results are from the experimental data essentially near the equilibrium. Comparing the computational results, they all tend to the same equilibrium value that is different from the experimental value; this may be explained by the inappropriatenessof the kinetic rate constants in the equilibrium area. The computational results differ essentially in the nonequilibrium area behind the shock wave. The main differences between the models are, on the one hand, the increasing slope of IR_{NO} behind the shock wave and, on the other hand, the level and the position of the maximum of IR_{NO}. Concerning the models that deal only with the coupling between the vibration and the dissociation, the very simple CVDV model gives results very close to those of the MFR model. As for the other models (Park, MFR, CVCV, and CVDEV), the corresponding curves are below those in the CVDV and MFR models. Among them, the CVDEV model with chosen values of U_D and U_E gives the lowest maximum value of IR_{NO}, and this maximum is the closest one to the experimental data. Moreover, the CVDEV model gives the smallest slope behind the shock: this is explained by the lag of the first exchange reaction that is led by the value of U_E. All of these remarks are valid for both mixtures. When comparing the results horizontally, the agreement between the computational results and the experimental data is better for the 60–40 mixture than for the 77.7–22.3 one. Nonetheless, if the values of the Knab CVCV parameters α and U had been adjusted, the corresponding results might have been closer to the experimental data than they are with the suggested values in Ref. 9. Note also that the MFR model was upgraded in 1996 by the introduction of the forced harmonic oscillator model.[12]

C. Quasi-One-Dimensional Computations of TCM2 Mach 6 Nozzle Flow

The steady one-dimensional code RELAX1D, first designed for flow relaxation behind normal or oblique shock waves, has been extended to nozzle flows. A computation has been performed in the TCM2 Mach 6 nozzle with different steps of the CVDV and CVDEV models to show the influence on the flow parameters. Figure 4 depicts the NO mass fraction distribution along the nozzle axis. Because the levels of Y_{NO} with the Landau–Teller model are the same as with the preferential or nonpreferential CVDV models,[10] only the curves corresponding to the preferential and nonpreferential CVDV and CVDEV models are plotted. When the coupling on the exchange reactions is taken into account (CVDEV model), the level of Y_{NO} is higher, and this level is even higher when the CVDEV is preferential (with $U_D = \theta_D/3.5$ and $U_E = \theta_A/10$). The rebuilding procedure of the nozzle exit conditions from the reservoir conditions, with the assumption of the flow driven by the CVDEV coupling model, leads to test section flow conditions close to equilibrium but still with vibrational nonequilibrium. Indeed, in the expanding nozzle flow, the vibrational temperatures are higher than the translational one, and therefore the exchange reaction coupling factors are greater than



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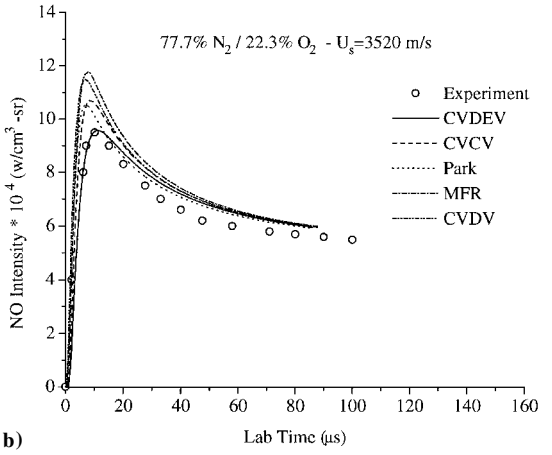

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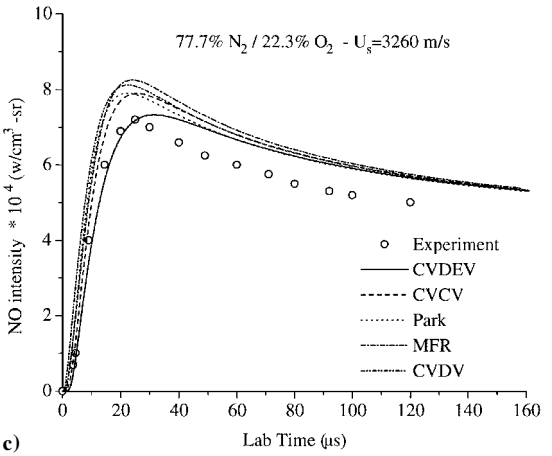

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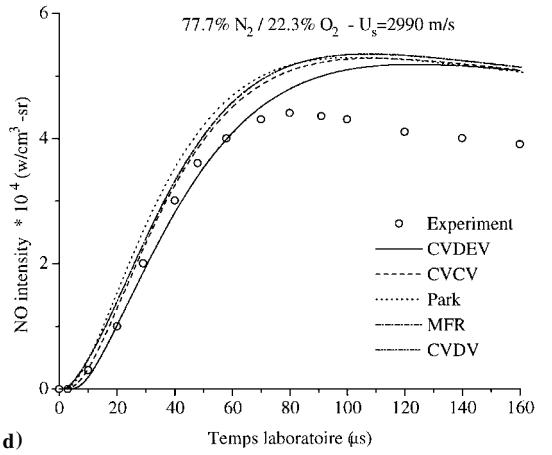
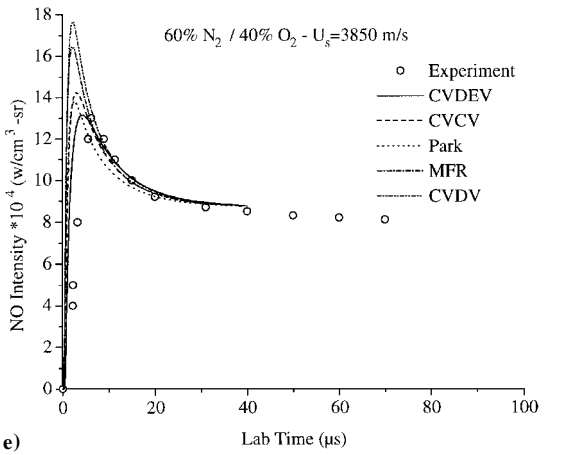


d)



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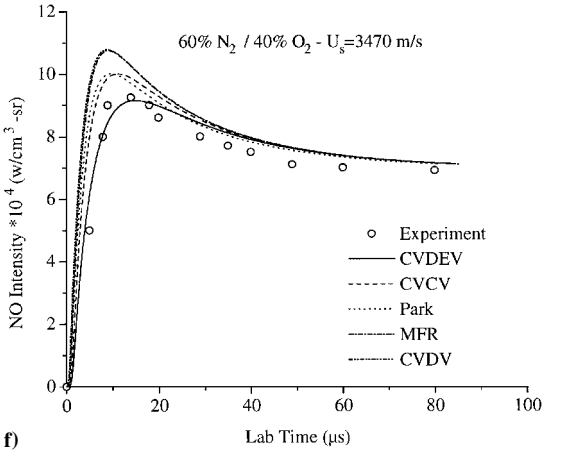

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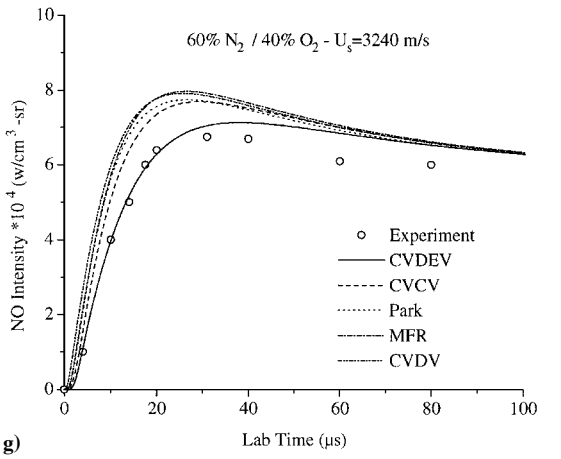

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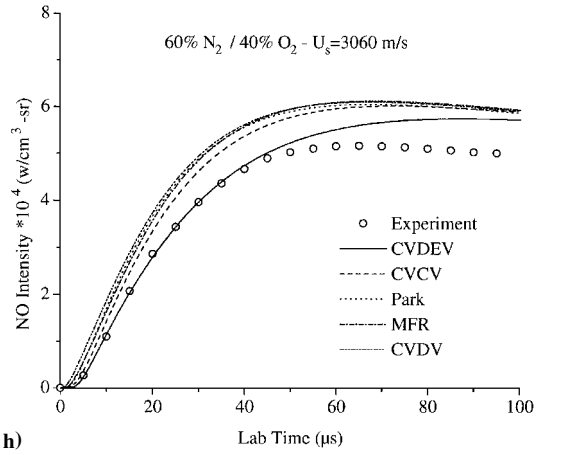

h)

Fig. 3 NO IR radiation profiles for different upstream velocities; P_∞ = 300 Pa.

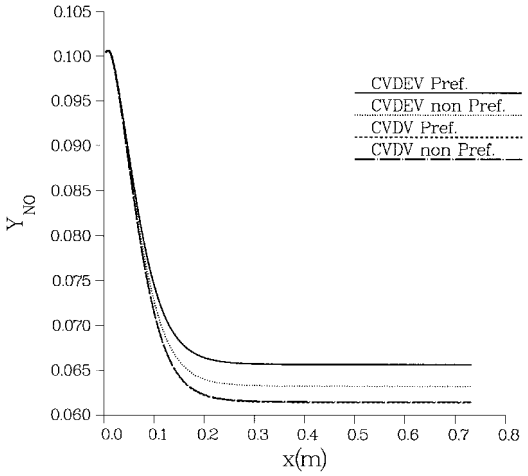

Fig. 4 TCM2 nozzle (P_0 = 225 bars and T_0 = 6500 K): Y_{NO}-axis distribution.

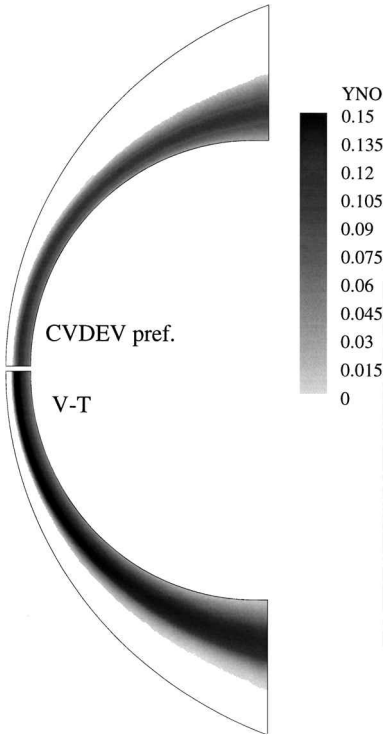

Fig. 5 Y_{NO} flowfield for Lobb sphere.

one, accelerating chemical relaxation in the nozzle. This tendancy is in good agreement with recent nozzle flow experimental results in the ONERA F4 wind-tunnel test section.[22]

D. Two-Dimensional Computations of the Flow Around a Sphere

In Fig. 5 the Y_{NO} flowfield around the Mach 15.3 Lobb sphere (diameter D = 12.7 mm) (Ref. 14) is presented. The comparison of the results obtained on the one hand with the preferential CVDEV model and on the other hand with no coupling (V-T exchanges only) shows that the levels of Y_{NO} behind the shock are different. Moreover, the nondimensional shock standoff distance δ/D obtained with different steps of the coupling and compared with data from Ref. 23 is reported in Table 2 and in Fig. 6. Here again, the preferential CVDEV result is the closest one to the experimental values.

As a last example of applications, Fig. 7 illustrates the stagnation line boundary-layer profiles of Y_{NO} for the Lobb sphere. These profiles have been obtained from the coupled Euler/defect boundary-layer approach.[15] The plots show the sensitivity of Y_{NO} behavior to the different models, in particular the change of slope in the boundary layer when preferentializing the CVDEV model.

Table 2 Nondimensional shock standoff distance

Models	δ/D
Tam et al.	0.041
Vib. equil.	0.04201
LT	0.04291
CVDEV	0.043867
CVDEV pref.	0.04572
Exp.	0.045

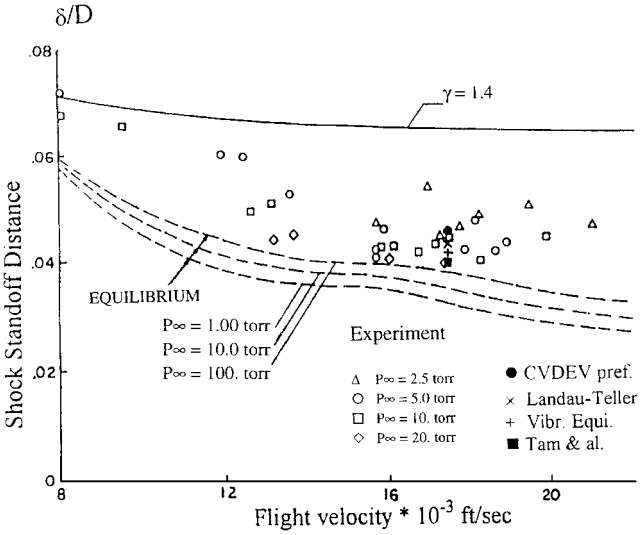

Fig. 6 Nondimensional shock wave standoff distances: comparisons between models.

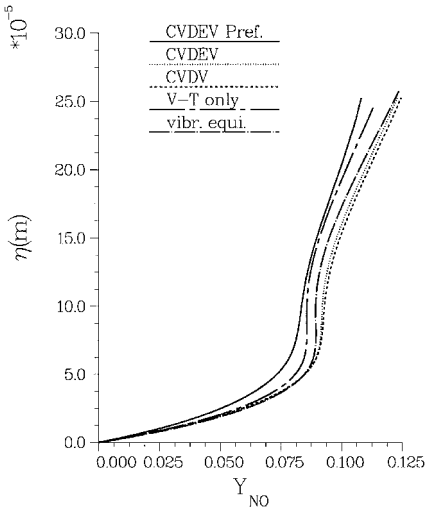

Fig. 7 Y_{NO} boundary-layer profiles along the stagnation line for Lobb sphere.

IV. Conclusions

A generalized preferential vibration-chemistry coupling (CVDEV) model has been presented, leading to the development of new expressions of the coupling factor V_E and of the additional vibrational source term ω_{EV}. It has been tested in one-dimensional and two-dimensional numerical simulations for external flows as well as for internal flows. The coupling effects resulting from this new model have been shown on the flow parameters behind a normal shock wave and compared with other numerical results and with experimental data. It follows that the results given by the CVDEV model with adjusted values of the variables U_D and U_E are in good agreement with NO infrared radiation experimental data in the particular cases treated here. Moreover, the different comparisons have shown that the level of NO behind the shock wave is determined by $U_{D_{O_2}}$ and $U_{E_{N_2}}$, which was not surprising because O_2 disappears essentially through the dissociation reactions and N_2 through the

exchange reaction. The influence of the CVDEV model has also been shown in flow computations in a nozzle, around a sphere, and in a boundary layer.

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