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State-to-state modeling of radiation coupled to vibration-translation relaxation and dissociation in nonequilibrium gas flows

A. Aliat,[1,*] P. Vedula,[1,*] and E. Josyula[2]
[1] *School of Aerospace and Mechanical Engineering, University of Oklahoma, Norman, Oklahoma 73019, USA*
[2] *U.S. Air Force Research Laboratory, Wright-Patterson Air Force Base, Dayton, Ohio 45433, USA*

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A radiation model is developed to obtain evolution of band intensities according to the state-to-state (STS) approach by considering vibration-translation and vibration-electronic jumps and dissociation. Investigation of the behavior of a nonequilibrium N_2 gas flow behind a shock shows that the radiation intensity remains weak and the flow is far from radiative equilibrium. Similar intensities are predicted by pure STS and hybrid approaches based on existing radiation models. However, the coupling between physicochemical and radiative processes increases with radiation intensity.

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Introduction. Although equations of aerothermochemistry that account for radiative effects have been considered by many authors [1–3], they are usually based on one-temperature or multitemperature assumptions and are often considered independently from the collision processes. This uncoupled description can imply noticeable errors in estimated values of radiation intensities and radiative heat flux in strongly nonequilibrium high-temperature reacting gas flows. To overcome this limitation, a state-to-state (STS) model was proposed in Ref. [4] on the basis of a rigorous kinetic theory with coupled vibrational relaxation, chemical reactions, and radiative transitions. The advantage of the STS approach is the lack of the assumption of quasistationary distributions over internal energies that is often used in the literature (multitemperature models) and is invalid for high-temperature conditions [5]. The equations of conservation of state-specific population, momentum, and energy developed in Ref. [4] contain radiative terms that allow for accounting of strong coupling between the physicochemical and radiative mechanisms. These radiative terms are governed by the microscopic radiative transfer equation that describes the evolution of specific intensity (i.e., the distribution function of photons) that is a spectral quantity. It is extremely challenging (from a numerical standpoint) to directly obtain this photonic distribution over the entire range of frequencies.

In this paper, we extend the theoretical study [4] by proposing a detailed model for radiation using an STS approach. In our model, the photonic distribution is obtained via the band intensities that are governed by a radiative transfer equation using a macroscopic approach. This model is implemented to generalize previous studies [5,6] and investigate the effects of radiation in a N_2 gas flow behind a plane shock wave, with the consideration of the dissociation of molecules and multiquantum vibration-translation (VT) and vibration-electronic (VE) transitions. The radiation from our pure STS approach is compared to that obtained from hybrid approaches where the radiative mechanisms are treated with commonly used (i) one-temperature (OT) and two-temperature (TT) assumptions (where as hydrodynamic variables are treated via STS approach) and (ii) the uncoupled form (where hydrodynamic and radiative conservation equations are independently treated). The influence of the radiation on the gas relaxation behind the shock is also investigated.

State-specific radiative model. For a one-dimensional (1D) stationary gas flow behind a normal shock, the microscopic radiative transfer equation reads [4]:

$$\frac{dI_\nu}{dx} = \sum_{\alpha,i,j,p,\alpha',i',j',p'} h\nu_{\alpha ijp,\alpha'i'j'p'}\,\varphi_\nu(\nu - \nu_{\alpha ijp,\alpha'i'j'p'}) \times [A_{\alpha ijp,\alpha'i'j'p'}N_{\alpha ijp} + (B_{\alpha ijp,\alpha'i'j'p'}N_{\alpha ijp} - B_{\alpha'i'j'p',\alpha ijp}N_{\alpha'i'j'p'})\,I_\nu], \tag{1}$$

where the variable x corresponds to the direction of the shock-wave propagation. Terms h and I_ν correspond to Planck's constant and specific intensity (based on frequencyν), respectively. The number density $N_{\alpha ijp}$is related to the quantum level of the electronic α, vibration i, rotational j and the parity p states. The primed (unprimed) letters in the above equation refer to the lower (upper) quantum level. Terms $B_{\alpha'i'j'p',\alpha ijp}$, $B_{\alpha ijp,\alpha'i'j'p'}$, and $A_{\alpha ijp,\alpha'i'j'p'}$ are the Einstein coefficients of induced absorption and induced and spontaneous emissions, respectively, which are related through the detailed balance principle, as $A_{\alpha ijp,\alpha'i'j'p'}/B_{\alpha ijp,\alpha'i'j'p'} = 2h\nu^3_{\alpha ijp,\alpha'i'j'p'}/c^2$ and $s_{\alpha ijp}B_{\alpha ijp,\alpha'i'j'p'} = s_{\alpha'i'j'p'}B_{\alpha'i'j'p',\alpha ip}$, where c is the speed of light. The term $s_{\alpha ijp}$ corresponds to the product of statistical weights related to rotational ($= 2j + 1$), vibrational ($= 1$ for diatomic molecules), and electronic s_α ($= (2 - \delta_{0,\Lambda}) \times (2S + 1)$) states. The factor $(2S + 1)$ corresponds to the spin multiplicity, while $(2 - \delta_{0,\Lambda})$ is the degeneracy due to the Λ-doubling. The Kronecker delta $\delta_{0,\Lambda}$ has a nonzero value equal to 1 only if $\Lambda = 0$, where Λ is the absolute value of the projected total electronic angular momentum on the internuclear axis that is equal to 0, 1, 2,... for $\Sigma, \Pi, \Delta, \ldots$ molecular states, respectively. The Einstein coefficient related to the spontaneous emission $\alpha,i,j,p \to \alpha',i',j',p'$ can be separated into two parts: $A_{\alpha ijp,\alpha'i'j'p'} = A_{\alpha i,\alpha'i'}S_{jp,j'p'}/2j + 1$, where $A_{\alpha i,\alpha'i'}$ is the Einstein coefficient for spontaneous emission related to the band transition $\alpha,i \to \alpha',i'$. The Hönl-London factors (or rotational line strengths) $S_{jp,j'p'}$ are related to branches

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[*] Corresponding authors: azizaliat@ou.edu; pvedula@ou.edu

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$jp \rightarrow j'p'$ and are normalized to obey the sum rule [7] as $\sum_{j',p'} S_{jp,j'p'} = (2-\delta_{0,\Lambda}\delta_{0,\Lambda'})(2S+1)(2j+1)$. The term ϕ_ν in Eq. (1) corresponds to the spectral line profile, which is assumed to be the same for the three kinds of radiative mechanisms (i.e., spontaneous emission and induced emission/absorption). This profile satisfies the normalization condition, i.e., $\int_0^\infty \phi_\nu(\nu - \nu_{\alpha ijp,\alpha' i' j' p'})d\nu = 1$, where $\nu_{\alpha ijp,\alpha' i' j' p'}$ is the central frequency of radiative transitions $\alpha,i,j,p \leftrightarrow \alpha',i',j',p'$.

In this study the radiative lines are assumed to follow the Doppler broadening (at low pressures and high temperatures) and do not overlap in the spectrum. Hence, from Eq. (1), properties on Einstein coefficients, Hönl-London factors, and the broadening profile, integrating over frequency and summing over the rotational levels (which follow a Boltzmann distribution with translational temperature T), the microscopic radiative transfer equation Eq. (1) can be expressed (at the macroscopic scale) as:

$$\frac{dI_{\alpha i,\alpha' i'}}{dx} = h\nu_{\alpha i,\alpha' i'} B_{\alpha i,\alpha' i'} N_{\alpha i}\left[\frac{2h\nu^3_{\alpha i,\alpha' i'}}{c^2} + \sqrt{\frac{\ln 2}{2\pi}}\frac{I_{\alpha i,\alpha' i'}}{\gamma^D_{\alpha i,\alpha' i'}}\left(1 - \frac{s_\alpha}{s_{\alpha'}}\frac{N_{\alpha' i'}}{N_{\alpha i}}\right)\right], \qquad (2)$$

which governs the evolution of the band intensity $I_{\alpha i,\alpha' i'}$ (power per area and per solid angle) behind the shock. The above equation is also obtained by assuming that the various branches emit on their mean central frequency that is the frequency of the corresponding band $\nu_{\alpha i,\alpha' i'}(= \tilde{\nu}_{\alpha ijp,\alpha' i' j' p'})$. The term $\gamma^D_{\alpha i,\alpha' i'}(= \nu_{\alpha i,\alpha' i'}\sqrt{2k_bT/mc^2})$ corresponds to the full width at half maximum of the Doppler line profile, which is also expressed according to the temperature T, the mass of the molecule m, and the constant of Boltzmann k_b. Note that the number density $N_{\alpha i}$ in Eq. (2) is related to the electrovibrational level (α,i).

We can compare our pure STS radiation model in Eq. (2) with hybrid models based on TT assumption often used in the literature. In this assumption, a Boltzmann distribution over vibrational energy at a vibrational temperature T_v is considered. This vibrational temperature is defined by the ratio of the two first vibrational levels in the ground electronic state, as these levels are the most populated and thus characterizes the thermodynamic evolution of the gas flow [8]. The TT model is obtained by implementing $N_{\alpha i} = N_\alpha \exp(-\varepsilon_i^\alpha/k_bT_v)/Q_\alpha^{vib}(T_v)$ in Eq. (2), where $Q_\alpha^{vib}(T_v)$ and $N_\alpha(=\sum_i N_{\alpha i})$ are the partition function of vibration (related to the electronic state α) at the vibrational temperature T_v and the number density of molecules on the electronic state α, respectively. The term ε_i^α corresponds to the energy of the vibrational level i of the corresponding electronic state α. The corresponding OT radiation model is obtained by considering above the translational-rotational temperature T instead T_v.

The nonequilibrium gas flow can be considered as a black body if it reaches the thermal (at the temperature T) and the radiative ($dI_{\alpha i,\alpha' i'}/dx = 0$) equilibrium. From this consideration, we can derive the following expression for the black-body band intensity:

$$I^{\mathrm{eq}}_{\alpha i,\alpha' i'} = \frac{2h\nu^3_{\alpha i,\alpha' i'}}{c^2}\gamma^D_{\alpha i,\alpha' i'}\sqrt{\frac{2\pi}{\ln 2}} \times \left[\frac{Q^{\mathrm{vib}}_\alpha(T)}{Q^{\mathrm{vib}}_{\alpha'}(T)}\exp\left(\frac{h\nu_{\alpha i,\alpha' i'}}{k_bT}\right) - 1\right]^{-1}. \qquad (3)$$

Radiative terms present in STS master equations [4] can be expressed from the band intensities $I_{\alpha i,\alpha' i'}$ obtained from Eq. (2). Using a similar approach to derive the macroscopic radiative transfer equation Eq. (2), the radiative source term present in the state-specific conservation equation [4] can be expressed as:

$$R^{\mathrm{rad}}_{\alpha i} \approx \frac{4\pi}{h}\left(\sum_{\alpha'',i''}\frac{1}{\nu_{\alpha'' i'',\alpha i}}\frac{dI_{\alpha'' i'',\alpha i}}{dx} - \sum_{\alpha',i'}\frac{1}{\nu_{\alpha i,\alpha' i'}}\frac{dI_{\alpha i,\alpha' i'}}{dx}\right), \qquad (4)$$

where the radiation field is assumed to be isotropic in this study; $\alpha''(\alpha')$ correspond to upper (lower) electronic levels compared to that α. Similarly, the derivative of the radiative heat flux in the total energy conservation equation [4] is such that:

$$\frac{dq_{\mathrm{rad}}}{dx} = \int_0^\infty \int_{4\pi}\frac{dI_\nu}{dx}\mathbf{\Omega}_\nu \cdot \mathbf{n}\, d\nu\, d\mathbf{\Omega}_\nu \approx 2\pi \sum_{\alpha,i,\alpha',i'}\frac{dI_{\alpha i,\alpha' i'}}{dx}, \qquad (5)$$

where $\mathbf{n}$ and $\mathbf{\Omega}_\nu$ are unit vectors along the direction of propagation of the shock and photon ν, respectively, and $d\mathbf{\Omega}_\nu$ is the corresponding solid angle.

Results and discussion. The present radiation model is implemented to generalize previous studies [5,6] for a pure N_2 gas flow behind a plane shock wave (1D steady Euler equations). The nitrogen molecules are considered to be in their ground ($X^1\Sigma$) and excited ($A^3\Sigma$ and $B^3\Pi$) electronic states, while undergoing the dissociation, VT, and VE energy exchanges. We use the VT and the dissociation models developed in Refs. [5] and [6] that are based on the forced harmonic oscillator (FHO) theory that accurately accounts for multiquantum jumps at high temperatures. These multiquantum jumps play a significant role in the evolution of intermediate and higher vibrational levels [5,6] that can have strong line strengths and thus can have a major part on the amount of emitted radiation. The first positive system of N_2 molecules is considered in this study and is described by spontaneous emissions $N_2(B^3\Pi,i) \rightarrow N_2(A^3\Sigma,i) + h\nu$ and induced emissions and absorptions $N_2(B^3\Pi,i) + h\nu \leftrightarrow N_2(A^3\Sigma,i) + 2h\nu$. A summary of spectroscopic data for the various electronic states of N_2 molecules can be found in Ref. [9], while the Einstein coefficients related to band transitions are given in Ref. [10]. The free stream conditions are those of Josyula *et al.* [11], i.e., a Mach number of 19.83, a temperature of 300 K, and a pressure of 27 Pa. A higher Mach number ($=25$) is also considered to make comparisons and study its influence on the numerical results.

The influence of the radiation on the molecular concentrations is shown in Fig. 1. It is clear that radiative mechanisms play a significant role on the concentration of $N_2(B^3\Pi)$

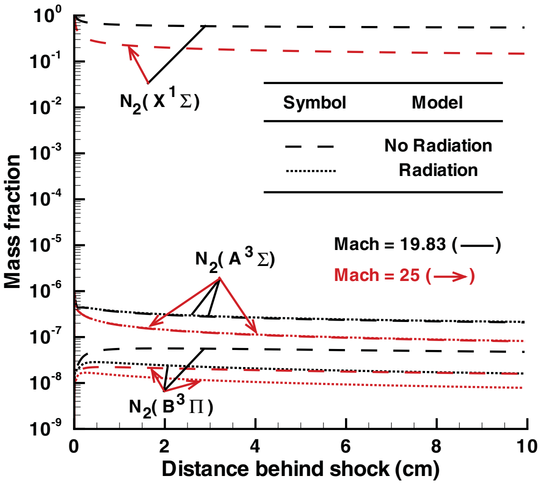

FIG. 1. (Color online) Concentrations of N_2 molecules behind the shock with and without the effects of the radiation at different Mach numbers.

molecules, as they correspond to upper levels of the first positive radiative system. Their concentration is found to be lower when the radiation is taken into account, due to radiative de-excitations to the lower electronic state $A^3\Sigma$. However, the number of these de-excitations is small compared to the population of $N_2(A^3\Sigma)$ molecules that remains nearly unchanged. With a higher Mach number, population of N_2 molecules (in their ground electronic state $X^1\Sigma$) decreases, especially from their intermediate and higher vibrational levels due the preferential character of the dissociation [6]. As the VE energy exchanges are connected to the population of these vibrational levels, the production of electronically excited molecules is thus decreased.

The intensity of radiation emitted by the gas flow remains low as shown in Fig. 2. This observation comes from weak excitation of N_2 molecules in the $B^3\Pi$ electronic state (see Fig. 1). The radiation intensity is thus mainly governed by spontaneous emissions (induced emissions and absorptions mechanisms play a minor part) which cause a constant decrease of the $N_2(B^3\Pi)$ population observed in Fig. 1. Figure 2 also shows that the gas flow cannot be considered as a black body, as the radiation intensity is ~6 orders of magnitude lower than that in a radiative equilibrium condition. The radiation is found to decrease with increase in Mach number since the production of emissive $N_2(B^3\Pi)$ molecules is less from VE transitions, as explained in the preceding paragraph.

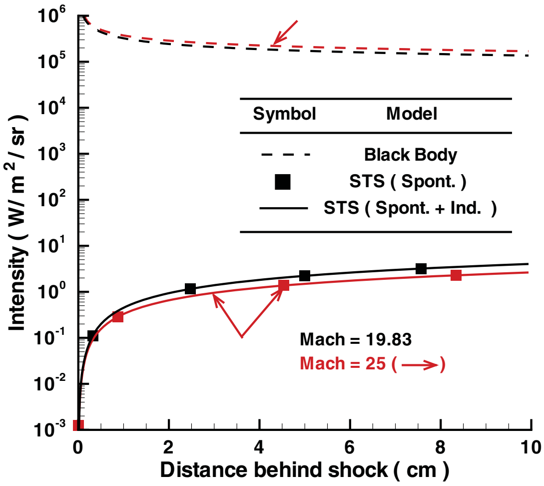

FIG. 2. (Color online) Radiation intensities behind the shock for different Mach numbers, obtained from black body and STS approaches with and without the consideration of induced emission and absorption mechanisms.

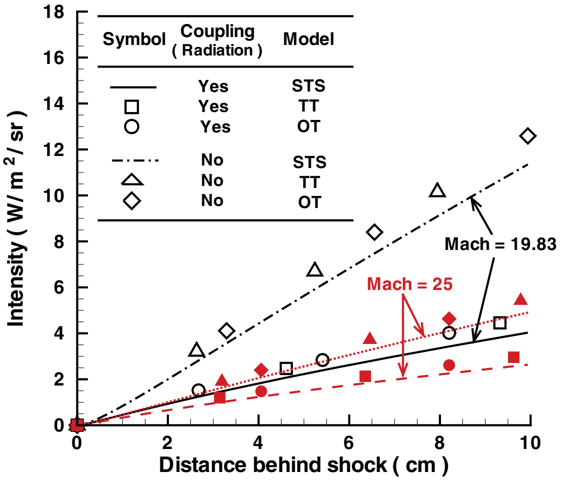

FIG. 3. (Color online) Radiation intensities behind the shock for different Mach numbers, obtained with and without the consideration of coupling between physicochemical and radiative processes based on STS, OT, and TT approaches. Note that the unfilled and filled symbols correspond to Mach 19.83 and 25, respectively.

The importance of coupling between the physicochemical and the radiative processes is observed in Fig. 3. The case without coupling tends to overestimate the emitted radiation and the discrepancy increases with its intensity. However, the radiation from the OT and TT models lead to similar intensities

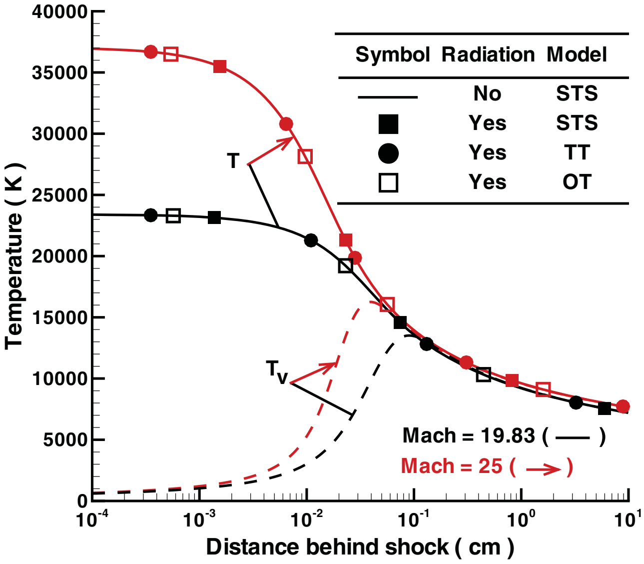

FIG. 4. (Color online) Translational-rotational and vibrational temperatures behind the shock with and without radiation based on STS, OT, and TT at different Mach numbers.

as that obtained with the STS approach. Small discrepancies observed between the approaches could come from of the weak intensity of radiation emitted from radiative transitions related to intermediate and higher vibrational levels. With a higher Mach, we have similar observations but with a weaker radiation due to the lower concentration of $N_2(B^3\Pi)$ molecules (see Fig. 1).

The radiation (from pure STS, OT, and TT approaches) has a minor influence on the translational-rotational temperature, as shown in Fig. 4. The evolution of the macroscopic gas parameters is essentially governed by the behavior of most populated species (i.e., on their ground electronic states) that do not contribute to the emitted radiation from the first positive radiative system. The evolution of the vibrational temperature shows that the OT and TT radiation models become similar in a ∼1 mm distance behind the shock. At a higher Mach, this distance is shorter (∼0.5 mm).

Conclusion. A detailed STS model for radiation is proposed by considering the spectroscopic properties (including fine structure, Einstein coefficients, Doppler broadening, Λ-doubling, the sum rule of Hönl-London factors) and is applied in computational fluid dynamics (CFD) modeling. This model is based on the radiative transfer equation to obtain the macroscopic band intensities (which are used to evaluate radiative terms in the hydrodynamic conservation equations in order to account for strong coupling between the physicochemical and radiative mechanisms). The STS, OT, and TT approaches are implemented to study the behavior of a radiative and reactive N_2 gas flow behind a plane shock. The first positive system of N_2 molecules is considered, i.e., radiative transitions between the excited electronic states $B^3\Pi$ and $A^3\Sigma$ (including spontaneous emissions and induced emissions/absorptions). Due to the effects of radiation, the concentration of $N_2(B^3\Pi)$ molecules decreases due to radiative de-excitations. The dominant contribution to radiation arises from spontaneous emissions (compared to induced mechanisms) because the radiation intensity remains weak in this study. The flow is far from radiative equilibrium and therefore cannot be treated as a black body. The influence of the coupling between the physicochemical and radiative processes increases according to the radiation intensity. Note that the commonly used OT and TT assumptions give predictions that are similar to that obtained from the STS approach. This observation can be attributed to weak radiation intensity obtained in this study. Radiation is found to decrease with increase in Mach number, as the preferential dissociation is more efficient which further lowers the production of electronically excited molecules from VE transitions. The radiative mechanisms have a minor influence on the evolution of macroscopic gas parameters such as the translational-rotational temperature, as they are primarily governed by the species in their ground electronic states.

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