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Nonequilibrium Dissociation Processes in Hyperbolic Atmospheric Entries

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Physical-chemical processes encountered behind atmospheric entry shock waves are known to occur in extremely nonequilibrium conditions. Also, translational temperatures up to 100,000 K may be reached immediately behind the shock wave. Such challenging conditions require the development of adequate state-to-state models, which prevents using widespread first-order theories. A complete database for the simulation of state-resolved dissociation processes is presented in this paper. Rate coefficients valid up to very high temperatures have been obtained for diatom–diatom collisions, using the forced harmonic oscillator theory. The rate coefficients for atom–diatom collisions have been selected after a critical review of the existing data sets, as the forced harmonic oscillator theory proved inadequate for the simulation of such processes. Such a consistent state-to-state model has then been used for simulating nitrogen dissociation processes behind very high-temperature shock waves, and the obtained results have been compared with those obtained using popular one- and two-temperature models.

Nomenclature

C = correction factor for N_2–N_2 rates
d = molecular diameter, m^2
E = level energy, Hz
$k(T)$ = thermal reaction rate, cm^3/s
k_B = Boltzmann constant, $1.3806505 \times 10^{-23}$ J/K
l = mean free path, m
n = species number density, m^{-3}
P = pressure, Pa
P = transition probability
T = macroscopic temperature, K
t = time, s
v = vibrational level
Z_2 = gas-kinetic two-body collisional frequency, Hz
Z_3 = gas-kinetic three-body collisional frequency, Hz
σ = collision cross section, m^2
τ_{VT} = characteristic vibration–translation relaxation time

Subscripts

diss = dissociation
f = final vibrational quantum number
i = initial vibrational quantum number
rec = recombination
tr = translational mode
VD = vibration–dissociation processes
vib = vibrational mode

I. Introduction

IMMEDIATELY behind an atmospheric entry shock wave, extreme nonequilibrium conditions are reached, and translational temperatures may achieve values as high as 100,000 K for high-speed hyperbolic entries. For a successful modeling of such strong disequilibrium conditions, resorting to a state-to-state approach is mandatory, as such conditions are outside the validity range of macroscopic or multitemperature models. Moreover, the relaxation processes encountered behind a shock wave follow different trends from the processes encountered in other nonequilibrium applications such as, for example, gas discharges or arc-jet flows. Therefore, adequate state-resolved methods have to be devised for the simulation of, among others, molecular vibration–vibration (V–V), vibration–translation (V–T), and dissociation processes in such flows.

This paper presents an investigation of shock-induced nitrogen dissociation processes, in view of the paramount importance of such process for the simulation of a spacecraft reentry in Earth's atmosphere. Here, we discuss the availability of adequate state-resolved reaction rates for simulating high-temperature nitrogen dissociation. Also, the adequacy of the available data sets is analyzed regarding a comparison of the corresponding thermal rates with available experimental data. Finally, utilizing the best available state-resolved rates, as well as popular one-temperature (T) and two-temperature models (T, T_{vib}), relaxation processes behind several high-temperature shocks are investigated.

II. Dissociation Rates from State-Resolved Models

The last 30 years have seen state-resolved models come into widespread use regarding the simulation of physical–chemical processes in different applications. State-resolved models have been applied with some success to the simulation of nonequilibrium processes in microwave or arc-jet facilities [1–8]. Regarding the simulation of shock-heated flows, the available studies are limited to one-temperature or multitemperature models [9–13], with some notable exceptions in which actual state-resolved models have been used [14–22].

Such lack of previous studies may be explained by the additional difficulties incurred when developing state-resolved models of shock-heated flows. Here, the flow species excitation occurs from heavy-impact processes, as opposed to electron-impact processes. Fundamentally, the large excess of the flow species translational energy results in very high velocity (energy) collisions occurring behind a shock wave. Such means that 1) collisional processes cannot be modeled according to perturbation theories, and 2) multiquantum transitions become nearly equiprobable to single-quantum transitions, preventing the use of ladder-climbing models for modeling shock-induced processes [8,16,17,23]. The use of first order perturbation theory, and namely the widespread SSH (Schwartz, Slawsky, and Herzfeld) approach [24,25] and its

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extensions [26–32], is therefore not feasible for the simulation of shock-heated flows.

Moreover, accounting for multiquantum transitions in the master equation requires 1) the calculation of a large set encompassing all possible transitions between the species internal levels, and 2) the inclusion of a large set of transition probabilities in the master equation, using considerably more computational resources. For atom–diatom V–T processes, one obtains a set of $(n+1)^2$ possible transitions, and for diatom–diatom V–V–T collisions, one obtains a larger set of $(n+1)^4$ possible transitions, where n represents the number of bound vibrational levels of the molecule. Such large number of considered V–V–T processes can, however, be reduced, as previous studies have shown that, for the conditions encountered behind a strong shock wave, the influence of such exchanges on the flow vibrational relaxation processes is limited [17,23,33]. Adamovich et al. have proposed neglecting purely V–V exchange processes, summing over all of the possible vibrational states of the collisional partner and using an equivalent V–T transition probability [17,23,34,35]:

$$P(i, \mathrm{all} \to f, \mathrm{all}) = P(i \to f) \qquad (1)$$

Taking into consideration such specificities of shock-heated flows, it is necessary to obtain a set of the overall multiquantum V–T rates, as well as a set of state-resolved dissociation rates, both valid up to 100,000 K. The most popular theories applicable to the simulation of state-resolved transitions in shock-heated flows include exact quantum models [36,37], semiclassical models such as the quasi-classical trajectory (QCT) method developed by Billing [38], and the analytical theory of the forced harmonic oscillator (FHO) [39–44].

Quantum and quasi-classical theories rely on the calculation of accurate potential energy surfaces (PES), to which a batch of trajectories is assigned through Monte Carlo methods. Such methods require the assignment of a considerable number of trajectories for a correct prediction of exchange processes with low-transition probabilities, and the calculation of accurate data sets may be computationally intensive. Alternatively, the analytical FHO method may be used. This method is capable of quickly determining transition probabilities for nonreactive transitions, but is restricted to one-dimensional collision trajectories [39–41], or alternatively to simplified three-dimensional collision trajectories [42–44]. In this sense, the model is less detailed than the former ones, but is, however, capable of predicting accurate transition probabilities and rates [23].

III. Dissociation Rates from Experiments

Experimental researches of shock-induced physical–chemical processes are carried out in ground-test facilities such as shock tubes [45–47] and are not exempt from difficulties. Compared to the steady-state flows seldom obtained in other facilities (microwave facilities, arc-jets), shock waves are transient flows with very short time scales. Consequently, shock-induced heavy-impact processes have been studied with less detail than electron-impact processes in other facilities. Typically, most of the obtained data consist only of thermal reaction rates or, at best, reaction rates considering an equilibrium vibrational temperature [48]. Nevertheless, a large number of experiments have been carried out regarding nitrogen shock-induced dissociation [49–55]. The obtained dissociation rates are roughly valid in the temperature range $T = [4000–15,000 \text{ K}]$. Such thermal dissociation rates have been reviewed, compiled, and extrapolated by several authors, who have included them in one-temperature chemical models [56–62]. The different rates for nitrogen dissociation are summarized in Table 1. The reaction rates for both collision partners (M = N2, N) are presented in Figs. 1 and 2, respectively, for the temperature range $T = [1000–100,000 \text{ K}]$

One possible way to refine and narrow the uncertainties of thermal dissociation is the analysis of the corresponding thermal recombination rates, linked to the dissociation rates through the detailed balance principle. Departing from the upper and lower bonds of the nitrogen dissociation rates plotted in Figs. 1 and 2, the detailed balance principle has been applied for determining the corresponding minimum and maximum bonds of atomic nitrogen three-body recombination.

Table 1 Rates for reaction $N_2 + M \to N + N + M$, cm^3/s

$M = N_2$	
Dunn & Kang [56]	$4.7 \times 10^{18} T^{-0.5} \exp(-113,000/T)$
Moss [57]	$4.8 \times 10^{17} T^{-0.5} \exp(-113,100/T)$
Gardiner [58]	$3.7 \times 10^{21} T^{-1.6} \exp(-113,200/T)$
Park [59,60]	$7.0 \times 10^{21} T^{-1.6} \exp(-113,200/T)$
Brenner [62]	$3.72 \times 10^{21} T^{-1.6} \exp(-113,000/T)$
Shatalov [61]	$2.97 \times 10^{15} T^{0.175} \exp(-112,910/T)$
$M = N$	
Dunn & Kang [56]	$4.085 \times 10^{22} T^{-1.5} \exp(-113,000/T)$
Moss [57]	$4.15 \times 10^{22} T^{-1.5} \exp(-113,100/T)$
Gardiner [58]	$1.6 \times 10^{22} T^{-1.6} \exp(-113,200/T)$
Park [59,60]	$3.0 \times 10^{22} T^{-1.6} \exp(-113,200/T)$
Brenner [62]	$1.11 \times 10^{22} T^{-1.6} \exp(-113,000/T)$
Shatalov [61]	$1.19 \times 10^{17} T^{-0.13} \exp(-112,982/T)$

A bibliographic survey has then been carried out to infer the availability of accurate recombination coefficients. Several measured recombination rates have been plotted against the maximum and minimum bounds of the recombination rates obtained by detailed balancing of Table 1 dissociation rates. Different data for the recombination reaction $N + N + N_2 \to N_2 + N_2$, as well as data from Clyne [63], are plotted in Fig. 3 [63]; data for the recombination reaction $N + N + N \to N_2 + N$ are plotted in Fig. 4.

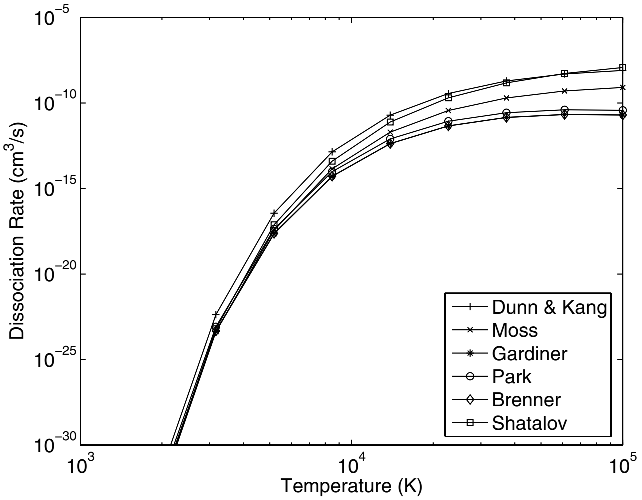

Fig. 1 Compared rates for the reaction $N_2 + N_2 \to N + N + N_2$.

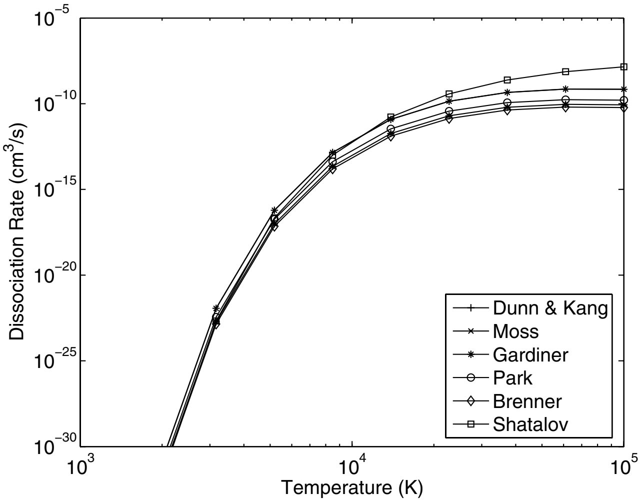

Fig. 2 Compared rates for the reaction $N_2 + N \to N + N + N$.

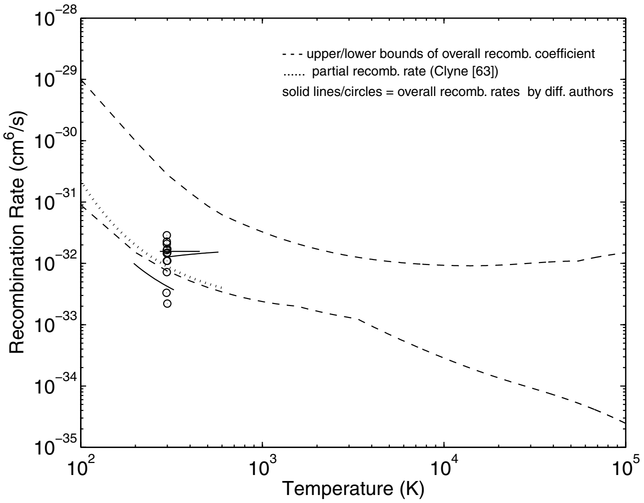

Fig. 3 Compared rates for the reaction $N + N + N_2 \rightarrow N_2 + N_2$.

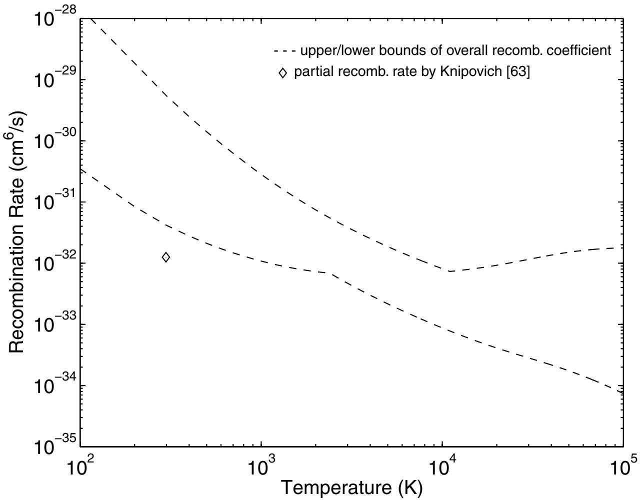

Fig. 4 Compared rates for the reaction $N + N + N \rightarrow N_2 + N$.

From the comparison of the different recombination rates, the large scattering of the data proposed for the reaction $N + N + N_2 \rightarrow N_2 + N_2$ only allows verifying that such data are closer to the lower bounds of the recombination rate. For the other reaction, the only available experimental data point is provided by Knipovich [64] for the $N + N + N \rightarrow N_2(B^3\Pi) + N$ partial recombination reaction, remaining below the lower bound of the overall recombination rate. For such temperature ranges, the lower bound of the overall recombination rate is given by the Shatalov [61] data set, which provides the best agreement with such measured recombination rates.

IV. Comparison of State-Resolved Data Sets for Nitrogen Dissociation

A. Rate Coefficients in N_2–N_2 Collisions

The first reliable rates for N_2–N_2 nonreactive diatom–diatom transitions have been provided by Billing and Fisher, who used a semiclassical method [65]. However, Billing and Fisher only provided V–T reaction rates up to the quantum vibrational number $v = 20$, and for a moderate temperature range with $T \leq 8000$ K. Therefore, the published data are insufficient for building a complete database of transition rates, as only V–T rates for the lower vibrational levels have been provided. Since then, Adamovich et al. [16] and the authors of this paper [23] have used the FHO theory to build a complete database of the overall multiquantum V–T transitions for N_2–N_2 collisions. Adamovich et al. [16] published analytical expressions for the calculation of the overall multiquantum V–T and dissociation rates, but in a previous work [23], some of the used asymptotical formulas have been verified to fail at predicting multiquantum transition probabilities at higher collision energies. In this previous work, V–T and dissociation rates in the whole vibrational range have been calculated. The energies of the 59 bound vibrational levels of the nitrogen molecule were determined through the reconstruction of the ground-state potential curve according to the RKR (Rydberg–Klein–Rees) method [66], relying on up-to-date spectroscopic data [67]. These have been fitted to a Dunham expansion:

$$\begin{aligned} E_{\mathrm{vib}} = {} & 2378.1(v + 1/2) - 18.516(v + 1/2)^2 \\ & + 0.26662(v + 1/2)^3 - 6.2127 \times 10^{-3}(v + 1/2)^4 \\ & + 3.4215 \times 10^{-5}(v + 1/2)^5 \end{aligned} \tag{2}$$

The state-resolved dissociation rates from such 59 levels have then been fitted to an analytical expression similar to the one proposed by Capitelli et al. [8]:

$$\log[k_{\mathrm{VD}}(T)] = a_0 + \sum_{i=1}^{4} a_i \exp(-T/b_i) \tag{3}$$

with

$$a_i = \sum_{j=0} Y_{ij} v^j \tag{4}$$

To provide an accurate fit, the data have been fitted in two temperature ranges of [300–5000 K] and [5000–100,000 K]. The fitting coefficients for these two ranges are presented in Table 2

The thermal dissociation rate predicted by our FHO model has then been compared with the experimentally determined dissociation rates. The contribution of the $N_2A^3\Sigma$ metastable electronic state has

Table 2 Fitting coefficients for N_2–N_2 collisions state-resolved dissociation rates, cm^3/s

$T_{\mathrm{tr}} = [300–5000\ \mathrm{K}]$						
		0	1	2	3	4
b_i			295.43	851.21	814.75	1610.7
Y_{ij}	1	−3.3208e + 1	−1.9020e + 2	−5.2638e + 1	−1.0556e + 2	−4.6484e + 1
	2	+6.5618e − 1	−6.1252e + 0	+2.5029e + 0	−8.4542e − 2	+1.0283e + 0
	3	+4.7942e − 3	−1.7693e − 1	+2.3483e − 1	+2.6388e − 1	−3.3590e − 2
	4	+2.9675e − 4	+1.6478e − 2	−2.4389e − 2	+1.4851e − 2	−8.8730e − 3
	5	−2.4707e − 5	−2.1618e − 4	−3.3026e − 4	+1.3770e − 4	+4.2279e − 4
$T_{\mathrm{tr}} = [5,000–100,000\ \mathrm{K}]$						
b_i			1884.0	12123.9	2144.4	12132
Y_{ij}	1	−1.0442e + 1	−5.1560e + 1	−1.1576e + 1	−2.3932e + 1	−1.1899e + 1
	2	+7.8328e − 3	−1.1825e + 0	+6.3523e − 1	+9.7714e − 1	+5.8941e − 1
	3	+1.6779e − 3	−2.3783e − 2	−2.4232e − 2	+1.2630e − 1	−3.3399e − 2
	4	−3.8547e − 5	+3.4510e − 3	−3.8990e − 4	−5.4565e − 3	+2.0911e − 3
	5	+1.5639e − 9	−5.0152e − 5	+1.8814e − 4	+5.4572e − 5	−2.1129e − 4

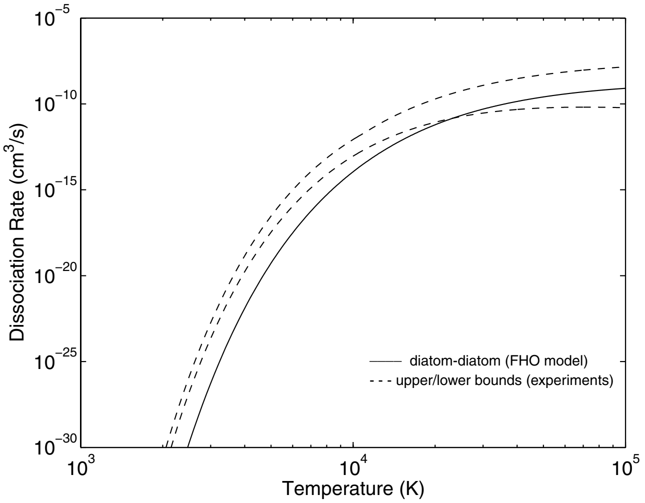

Fig. 5 Comparison of dissociation rates obtained from FHO model and experiments.

been estimated [68] to account approximately for twice the contribution of the ground state. The dissociation rate predicted by the FHO model for the nitrogen ground state has therefore been multiplied by a factor of three to account for the contribution from this metastable. The comparison between the different dissociation rates is presented in Fig. 5.

From such a comparison, it is verified that the dissociation rates predicted by the FHO model fall one to three orders of magnitude lower than the experimental rates (depending on the temperature range), although both experimental and FHO rates agree very well qualitatively. For higher temperatures, such an underprediction might be a consequence of not considering the contribution of the additional N_2 excited electronic states (other than the $A^3\Sigma$ metastable) to the overall dissociation rate. However, this is no longer true at lower temperatures where the contribution from excited electronic states will be negligible. Furthermore, above 10,000 K, the dissociation rates predicted by the FHO model approach the experimentally predicted rates, the discrepancies being less marked in such temperature ranges. Instead, such discrepancies are likely to result from a slight underprediction of the transition rates of the higher-lying levels. A comparison of monoquantum V–T deactivation rates between the two models is shown in Fig. 6. Transitions $1 \rightarrow 0$, $10 \rightarrow 9$, and $20 \rightarrow 19$ are displayed from right to left. It is verified that for increasing vibrational quantum numbers, the predicted FHO transition rates start diverging from the rates predicted by Billing and Fisher [65], the former rates being lower than the latter. Such discrepancies may result from an approximate treatment of the effects of molecular rotational, as our one-dimensional FHO model resorts to steric factors to account for such effects, instead of resorting to a more detailed three-dimensional collision model.

From a qualitative analysis of the experimental and FHO rate trends, it is found that the experimental rate proposed by Shatalov [61] agrees the best with the thermal reaction rate predicted by the FHO model. A simple engineering approach for obtaining a better agreement with experimental data, similar to the one used in a work by Park [69], would be to apply an identical correction factor for the overall state-resolved dissociation rates. This correction factor has been determined to have the following expression

$$C = 0.1278 \times 10^{(170/\sqrt{T})} \tag{5}$$

Care should be exerted, however, when applying such a correction factor. Although such an empirical correction factor may improve the accuracy of reaction rates between higher-lying levels, the opposite is true for rates between lower-lying levels, which may be overestimated using such a correction factor (see Fig. 6). One therefore needs to choose among having accurate transition rates between lower-lying levels at the cost of slightly underestimated dissociation rates, or having accurate dissociation rates at the cost of slightly underestimated transition rates between lower-lying levels.

B. Rate Coefficients in N_2–N Collisions

Nitrogen atom–diatom processes have been the subject of more focus than diatom–diatom processes, with several published works from different research teams. The study of such processes in nitrogen has been pioneered by Laganá et al. who proposed a PES for the reaction [70,71], and published a set of V–T rates up to the vibrational level $v = 45$. As state-resolved dissociation rates were not provided by Laganà, a complete database of transition rates has been developed (including state-resolved dissociation rates), using a Morse intermolecular potential, based on Laganà's PES. The comparison between our calculated rates and the rates published by Laganà shows reasonable agreement, as presented in Fig. 7.

However, upon determining the corresponding thermal dissociation rates, as provided by the FHO model, it was verified that it largely exceeded the experimentally determined rates at lower temperatures. Such effects in the FHO model are due to the large attractive potential well of the used Morse function (18,100 K), resulting in large transition rates, even at lower translational temperatures. Although the dissociation rates predicted by the FHO remain below the two-body kinetic rate, they are not even physically correct, as they violate the principle of detailed balance: at lower temperatures, the application of such principle yields recombination rates many orders of magnitude above the three-body collision rate.

In Fig. 8, we have plotted the N_2–N dissociation rate predicted by the FHO model, the two-body kinetic rate Z_2, and the maximum

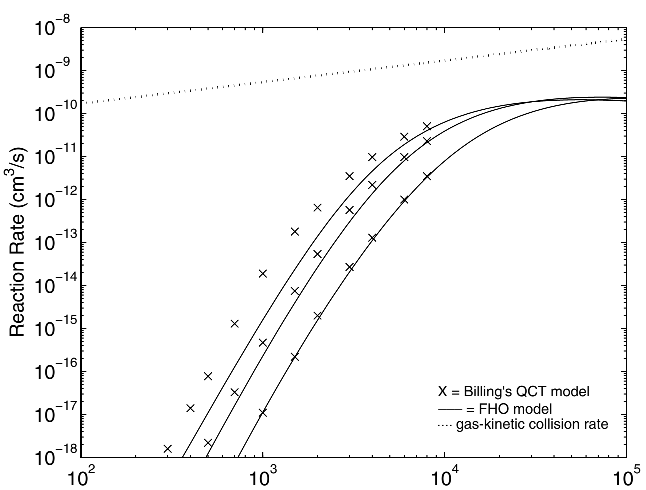

Fig. 6 Comparison between the single-quantum V–T transition rates.

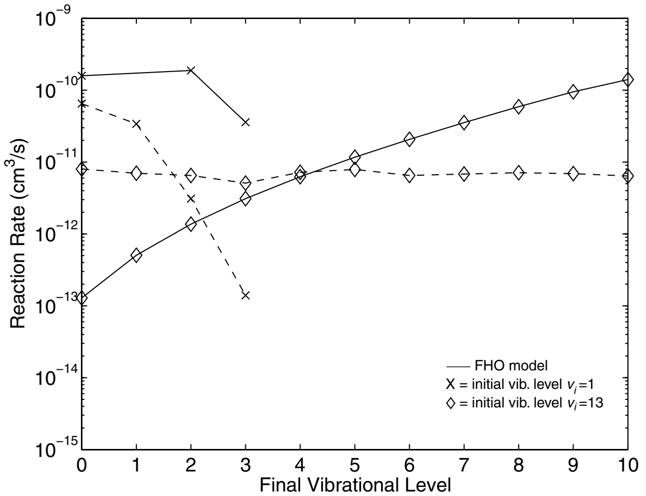

Fig. 7 Comparison between the reaction rates at a translational temperature of 1000 K.

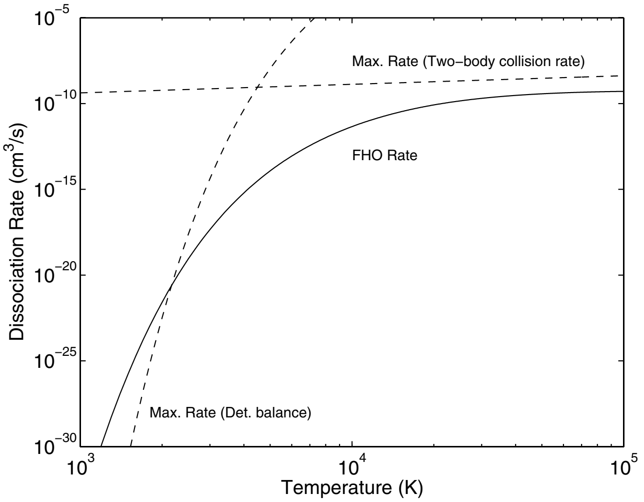

Fig. 8 Comparison between the N_2–N dissociation rate with the collisional limit rates.

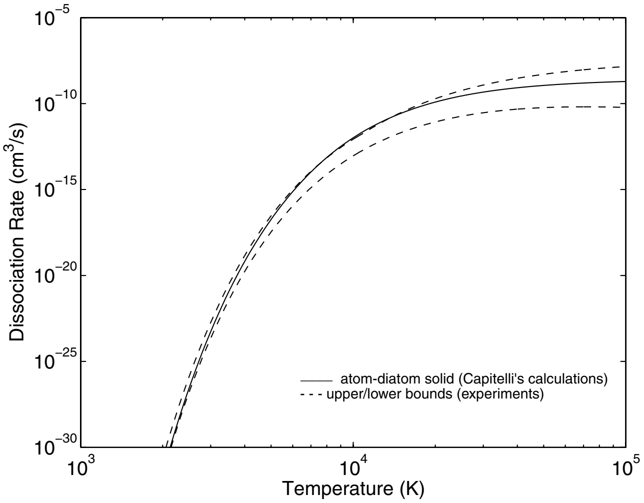

Fig. 9 Comparison of atom–diatom thermal dissociation rate and experimentally determined dissociation rates.

dissociation rate allowed by detailed balancing of the three-body collision rate Z_3. The three-body collision rate has been determined from the two-body collision rate according to the relationship

$$Z_3 = Z_2 \frac{d}{l} = Z_2 \frac{8\sigma^3}{\pi} n \tag{6}$$

with $\sigma = 28$ Å^2. The three-body collisional rate depends on the local density of the flow, and, as a minorant, we have considered a gas pressure of 1 Pa.

We can see that for such pressures, the dissociation rate predicted by the FHO model exceeds the allowed bounds for temperatures below 2000 K. Therefore, it is concluded that the FHO model cannot be accurately applied to the prediction of state-resolved transition rates for nitrogen atom–diatom collisions. However, the adequate agreement with the QCT rates predicted by Laganà et al. [70,71] (see Fig. 7) shows that these latter results may also be overestimated. Further comparisons with QCT calculations from Esposito and Capitelli [72,73], which relied on this same PES, also showed adequate agreement with the FHO model results. One possible explanation for the aforementioned discrepancies would therefore be the inadequacy of the used intermolecular potentials. Indeed, a different PES has been proposed by Wang et al. [74,75] who applied a fully quantal method to determine a limited array of state-resolved rates for exchange reactions. The comparisons carried with the state-resolved rates published by Esposito and Capitelli [72,73] showed that the newly predicted rates were considerably smaller, and such differences were claimed to be explained by a lowering of the effective barrier height on the PES, as a result of tunneling effects accounted for by the used quantal model. Recently, however, the PES published by Laganá et al. [70,71] has been once more selected by Capitelli et al. [8] who have carried a refined QCT calculation to yield more accurate reaction rate coefficients. The new techniques described in their paper [8] included a larger batch of assigned trajectory calculations and a careful crosscheck of the calculated trajectories, and it was verified that the predicted transition rates were significantly lower than previous rates based on the same PES. The contribution of the excited electronic states to the overall dissociation has also been considered in their model, using a simplified approach. An analytical expression for the calculation of the state-resolved dissociation rates has been provided and, taking into account the expression for the different 67 vibrational levels considered in the model [76], the calculation of the corresponding thermal dissociation rate can be carried. The comparison of this rate with the experimental dissociation rates previously discussed is presented in Fig. 9.

From the comparison of the calculated thermal dissociation rate with the experimental data, it is verified that an excellent agreement is reached for all the temperature ranges. Namely, the calculated dissociation rate matches very closely the experimental dissociation rate proposed by Shatalov [61]. Such a result proves the adequacy of the PES proposed by Laganà et al. [70,71] for accurately predicting N_2–N collisional processes. Furthermore, one may conclude that a semiclassical approach is sufficient for treating such collisional processes, without the need to resort to a fully quantum treatment such as proposed by Wang [74,75]. However, the FHO theory has been verified to be inadequate for the simulation of such collisional processes. Such a failure, compared with the relative good agreement reached for N_2–N_2 collisions, may be a consequence from a failure of the FHO theory to adequately reproduce molecular interactions with large attractive parts.

V. Shock-Induced Processes Simulation from Macroscopic and State-Resolved Models

Taking into account the state-resolved N_2–N_2 reaction rates proposed here (without the correction factor) and the N_2–N reaction rates proposed by Esposito & Capitelli [72,73], several time-dependent simulations of shock-induced processes have been carried. Three different postshock translational temperatures of 20,000, 50,000, and 100,000 K have been considered. To analyze the discrepancies between the results predicted within the present state-to-state formulation and the usual macroscopic approaches, further calculations of the same problem have been carried out using a one-temperature model and a two-temperature model, accounting for the macroscopic dissociation rates predicted by Shatalov [61].

For the state-to-state approach, the usual master-equation has been used:

$$\begin{aligned}\frac{dN_2(v_i)}{dt} &= \sum_{M=N_2,N} (K_{ji})_M N_2(v_j)M - (K_{ij})_M N_2(v_i)M \\ &\quad + (K_{\mathrm{rec},i})_M N^2 M - (K_{\mathrm{diss},i})_M N_2(v_i)M\end{aligned} \tag{7}$$

Energy conservation has been enforced in the usual way:

$$\frac{5}{2}k_B T_{\mathrm{tr}} \frac{dN_2}{dt} + \sum_i E_{\mathrm{vib}}(v_i)\frac{dN_2(v_i)}{dt} + \left(\frac{6}{2}k_B T_{\mathrm{tr}} + E_{\mathrm{dis}}\right)\frac{d2N}{dt} = 0 \tag{8}$$

For the two-temperature model, the usual Landau–Teller expression has been used for calculating vibrational relaxation:

$$\frac{dE_{\mathrm{vib}}}{dt} = \frac{E_{\mathrm{vib}}(T) - E_{\mathrm{vib}}(T_v)}{\tau_{\mathrm{VT}}} \tag{9}$$

with $\tau_{\mathrm{VT}} = \tau_{\mathrm{MW}} + \tau_{\mathrm{Park}}$ in which τ_{MW} is the characteristic relaxation time proposed by Millikan and White [77], and $\tau_{\mathrm{Park}} = N\sigma_{\mathrm{vib}}Z_2$ is the collision-limiting time as proposed by Park [78] with $\sigma_{\mathrm{vib}} = 3 \times 10^{-21}(5 \times 10^4/T)^2$.

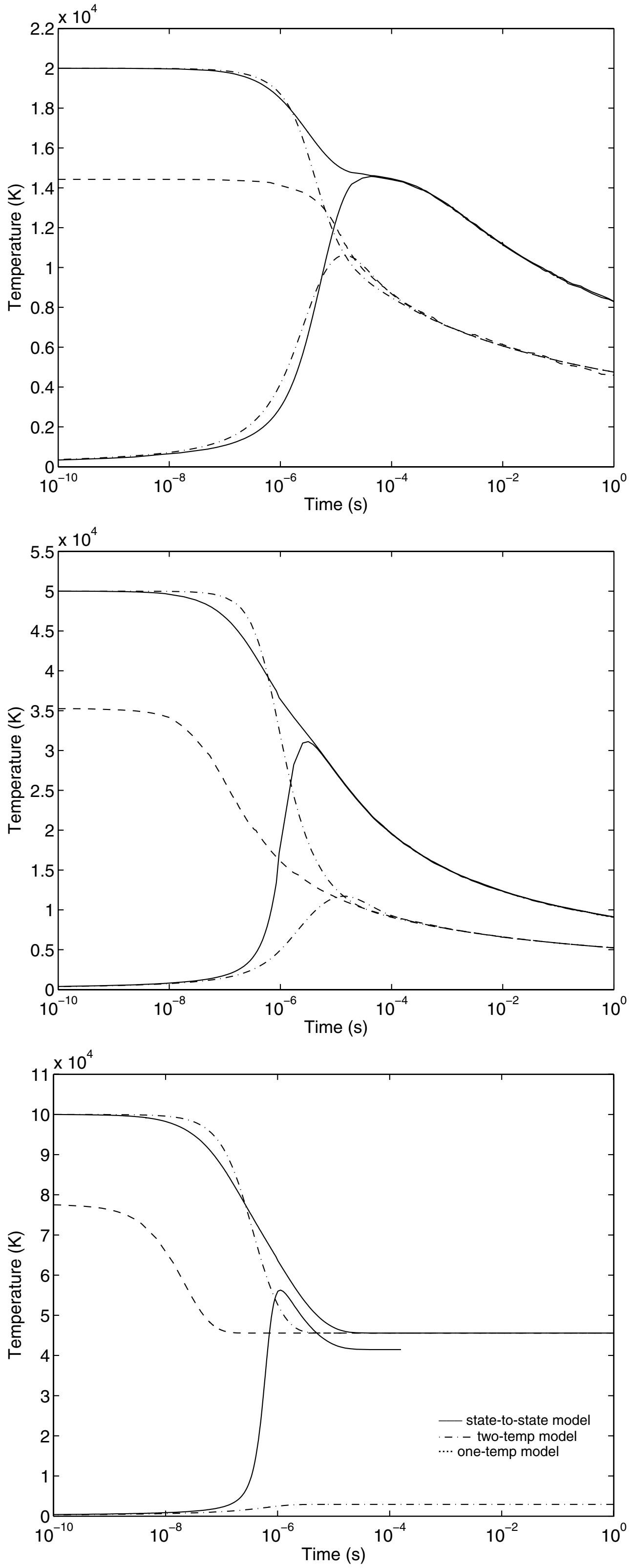

Fig. 10 Temperature relaxation behind a shock wave at 20,000, 50,000, and 100,000 K.

For nitrogen we have

$$\tau_{\mathrm{MW}} = \exp[72.4(T^{-\frac{1}{3}} - 0.015) - 18.42]\frac{101325}{P} \tag{10}$$

Finally, for the two-temperature model a geometrical temperature $\sqrt{TT_{\mathrm{vib}}}$ is considered in the dissociation rates calculations accounting for vibrational effects on dissociation processes.

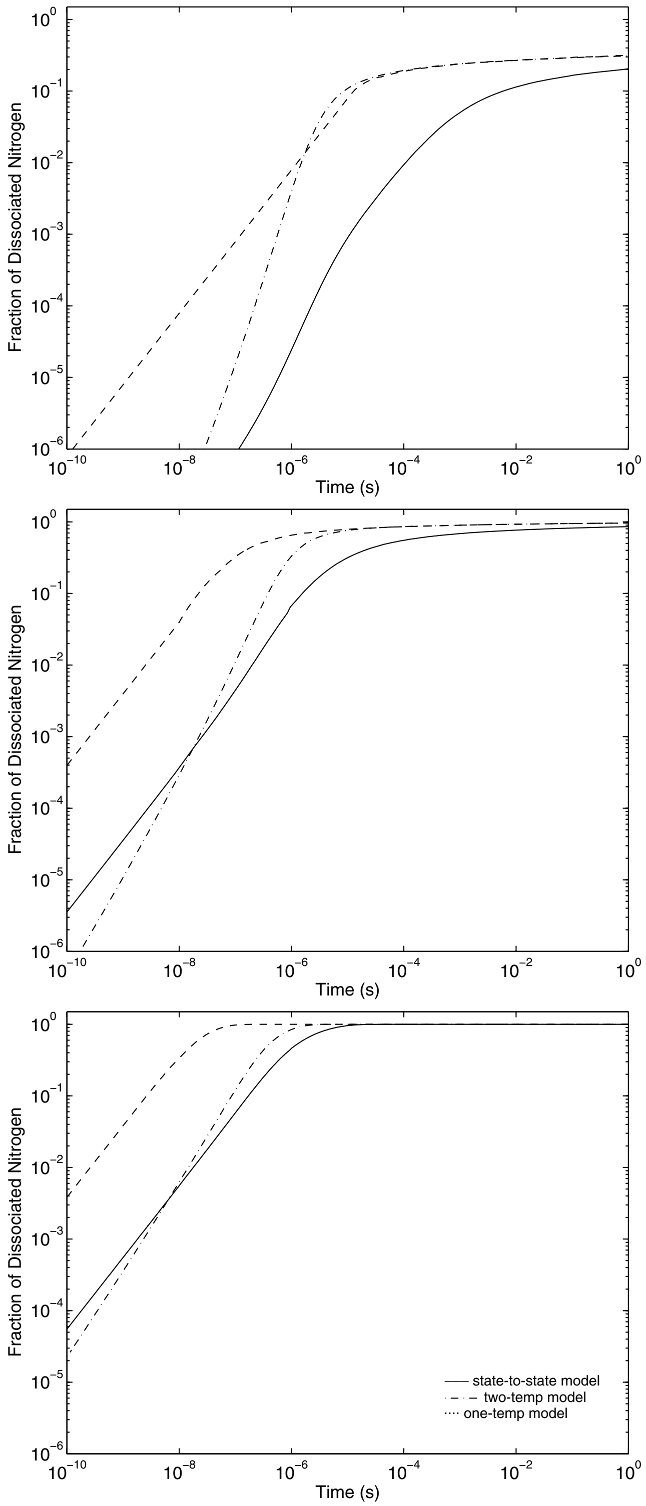

Fig. 11 Fraction of dissociated nitrogen behind a shock wave at 20,000, 50,000, and 100,000 K.

The obtained results are presented in Figs. 10 and 11. Here, the relaxation of the translational and vibrational temperatures (first vibrational temperature for the case of the state-to-state approach), as well as the time evolution of dissociation processes is depicted.

For the three approaches, differences are clearly apparent. The one-temperature model relies solely on the translational temperature, and therefore overestimates dissociation processes. Even when comparing two-temperature and state-resolved models, the differences are largely apparent. Overall, relaxation and dissociation processes predicted by the two-temperature model are quicker than those predicted by the state-to-state model.

The relaxation processes predicted by the state-to-state approach are systematically slower than those predicted by macroscopic models. Interesting enough, at higher temperatures (100,000 K), the difference is less apparent. This is not surprising, as for such temperatures, direct-dissociation from the lower levels can occur very easily, and the ladder-climbing phenomena, responsible for the existence of an incubation time before dissociation triggering, is less important in this case. At 100,000 K, translation–vibration equilibrium is not even achieved in the state-to-state and two-temperature approaches. Before this can happen, nitrogen molecules are almost totally dissociated into atomic nitrogen.

In brief, large discrepancies are found between the state-to-state approach and popular macroscopic models. Consequently, a state-to-state approach may indeed be mandatory for an accurate simulation of hyperbolic atmospheric entries.

VI. Conclusions

From the application of the FHO model to the simulation of N_2–N_2 collisions, and the application of the QCT model as developed by Esposito and Capitelli [72,73], an adequate set of state-resolved rate coefficients is available for the simulation of physical–chemical processes in shock-heated nitrogen flows. This set has been used for simulating high-temperature shock waves, and the results have been compared with those obtained using one- and two-temperature models. It has been verified that the results obtained using either of these three approaches differed very significantly from the other ones. Interesting enough, at extremely high temperatures, the results obtained according to a state-to-state approach become close to the ones calculated using a two-temperature approach. Physically speaking, direct-dissociation processes overcome pure V–T processes responsible for the ladder-climbing phenomena. Such phenomena cannot be adequately captured by theoretical models assuming Boltzmann distributions of vibrational levels such as the two-temperature model used here, which explains why the discrepancies against the state-to-state approach are considerable, except at 100,000 K.

An adequate database for the simulation of state-resolved processes has been successfully built and tested. Further developments of such database will require the inclusion of interactions with other species such as atomic and molecular oxygen, and also an explicit treatment of interactions with atomic and molecular electronic levels. The database presented here represents a first step toward the definition of an accurate and complete collisional-radiative model for the simulation of high-speed atmospheric entries.

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