Rovibrational Internal Energy Transfer and Dissociation of High-Temperature Oxygen Mixture

Sung Min Jo,^1 Simone Venturi,^1 Jae Gang Kim,^2 and Marco Panesi^1,*

^1) Center for Hypersonics and Entry Systems Studies (CHESS), University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

^2) Department of Aerospace System Engineering, Sejong University, Seoul 05006, Republic of Korea

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This work constructs a rovibrational state-to-state model for the O$_2$+O$_2$ system leveraging high-fidelity potential energy surfaces and quasi-classical trajectory calculations. The model is used to investigate internal energy transfer and non-equilibrium reactive processes in dissociating environment using a master equation approach, whereby the kinetics of each internal rovibrational state is explicitly computed. To cope with the exponentially large number of elementary processes that characterize reactive bimolecular collisions, the internal states of the collision partner are assumed to follow a Boltzmann distribution at a prescribed internal temperature. This procedure makes the problem tractable, reducing the computational cost to a comparable scale with the O$_2$+O system. The constructed rovibrational-specific kinetic database covers the temperature range of 7500-20,000 K. The reaction rate coefficients included in the database are parameterized in the function of kinetic and internal temperatures. The analysis of the energy transfer and dissociation process in isochoric and isothermal conditions reveals that significant departures from the equilibrium Boltzmann distribution occur during the energy transfer and dissociation phase. Comparing the population distribution of the O$_2$ molecules against the O$_2$+O case demonstrates a more significant extent of non-equilibrium characterized by a more diffuse distribution whereby the vibrational strands are more clearly identifiable. This is partly due to a less efficient mixing of the rovibrational states, which results in more diffuse rovibrational distributions in the quasi-steady-state distribution of O$_2$+O$_2$. The master equation analysis for the combined O$_3$+O$_4$ system reveals that the O$_2$+O$_2$ governs the early stage of energy transfer, while the O$_2$+O takes control of the dissociation dynamics. The findings achieved by the present work will provide strong physical foundations exploitable to construct an improved reduced-order model for oxygen chemistry.

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a) Electronic mail: mpanesi@illinois.edu
I. INTRODUCTION

Behind strong shock waves, diatom-diatom collisions are essential as they initiate the dissociation process and determine the chemical production rates of atomic species. Once a significant number of atoms are created, atom-diatom processes govern the thermochemical non-equilibrium state of the gas\(^1\)\(^{11}\). In hypersonic flows within Earth’s atmosphere, \(\mathrm{O}_2+\mathrm{O}_2\)\(^5\)\(^\text{12}\), \(\mathrm{O}_2+\mathrm{N}_2\)\(^3\)\(^\text{10}\), and \(\mathrm{N}_2+\mathrm{N}_2\)\(^1\)\(^\text{10}\) are the relevant diatom-diatom systems. Among them, \(\mathrm{O}_2+\mathrm{O}_2\) interaction provides the focus of the present work, owing to its dominant contribution to the early stage of thermochemical relaxation, justified by the weak bond energy of molecular oxygen.

The \(\mathrm{O}_2+\mathrm{O}_2\) system has been investigated extensively, both experimentally\(^7\)\(^{11}\) and numerically\(^5\)\(^{12}\)\(^{16}\). Recently, shock tube experiments were carried out by Ibraguimova et al.\(^11\) and Streicher et al.\(^7\) to measure vibrational relaxation times and non-equilibrium dissociation rate coefficients. Those measurements provided are mainly used as a reference for validating models. Theoretical calculations\(^5\)\(^{12}\)\(^{16}\) of the \(\mathrm{O}_2+\mathrm{O}_2\) system include approximate and high-fidelity estimates. Lino da Silva et al.\(^12\) proposed a vibrational-specific (VS) state-to-state (StS) model constructed using the Forced Harmonic Oscillator (FHO) theory and one-dimensional Morse inter-molecular potential. Andrienko and Boyd\(^13\) devised another VS model using the quasi-classical trajectory (QCT) method. In their work\(^13\), a double many-body expansion (DMBE) potential energy surface (PES) developed by Varandas and Pais\(^14\) was used to describe molecular interactions. The major shortcoming of these studies\(^12\)\(^13\) is the crude treatment of rotational degrees of freedom, assumed to be in equilibrium at the translational energy. The previous works\(^12\)\(^17\) demonstrated that the rotational non-equilibrium is essential to model hypersonic shock layers accurately. Grover et al.\(^6\) performed the direct molecular simulation (DMS) using the \textit{ab-initio} PESs proposed by Paukku et al.\(^15\)\(^16\). The results of Grover et al. accounted for the rotational non-equilibrium and showed good agreement with the available experimental data. Although the DMS simulation captured general aspects of non-equilibrium kinetics in the \(\mathrm{O}_2+\mathrm{O}_2\) system, the method cannot capture the details of the rovibrational-specific population dynamics, which is still unknown to the author’s best knowledge. Understanding the rovibrational distributions and their dynamics in time is crucial to developing an advanced reduced-order model for non-equilibrium thermochemistry\(^2\)\(^18\).
The numerical simulation of the rovibrational-specific molecular interactions in the \( \text{O}_2+\text{O}_2 \) system is computationally prohibitive. Several efforts have been made to model the rovibrational energy transfer and non-equilibrium dissociation in 4-atom systems. Kim and Boyd\cite{Kim2019} employed an ordinary Kriging model to estimate fully rovibrational-specific StS rate coefficients in the \( \text{H}_2+\text{H}_2 \). In another paper, Kim \textit{et al.}\cite{Kim2020} proposed an approximated treatment of the internal states, assumed to be populated according to a Boltzmann distribution of one of the molecules in the \( \text{H}_2+\text{H}_2 \) system to reduce the computational complexity. Macdonald \textit{et al.}\cite{Macdonald2010} developed a coarse-grain QCT (CG-QCT) method to investigate non-equilibrium rovibrational energy transfer and dissociation in \( \text{N}_2+\text{N}_2 \) by relying on a binning strategy among internal states. Following Kim \textit{et al.}\cite{Kim2020}, the present work proposes to model rovibrational energy transfer and dissociation in the \( \text{O}_2+\text{O}_2 \) system, assuming a thermal distribution for a collision partner.

Toward this end, the present study proposes a hybrid strategy to model the rovibrational-specific interactions in the \( \text{O}_2+\text{O}_2 \) system by extending the modeling concepts by Kim \textit{et al.}\cite{Kim2020}. This procedure imposes a single energy bin on the colliding molecule that is Boltzmann distributed at a prescribed internal temperature. At the same time, the target \( \text{O}_2 \) contains complete information on the rovibrational states. The present model is built on the framework consisting of the QCT method and master equation analyses. The QCT simulations employ the \textit{ab-initio} PESs by Paukku \textit{et al.}\cite{Paukku2015,Paukku2016} to construct a rovibrational-specific StS kinetic database. Then the master equation analysis was performed in the kinetic temperature range of 7500-20 000 K. The rovibrational-specific population dynamics, energy transfer, and dissociation are thoroughly investigated to understand the fundamental physics behind the \( \text{O}_2+\text{O}_2 \) collisional system. A direct comparison with a VS model, which this work has also constructed, is made. In addition, the underlying physics in the rovibrational distributions of the \( \text{O}_2+\text{O}_2 \) system is directly compared with that of \( \text{O}_2+\text{O} \) to make clear differences between them. Finally, the master equation study is extended to the combined \( \text{O}_3 \) and \( \text{O}_4 \) systems (\textit{i.e.}, \( \text{O}_2+\text{O} \) and \( \text{O}_2+\text{O}_2 \)) to identify their relative contributions.

This paper is organized as follows: The cost-effective modeling strategy to evaluate rovibrational distributions in the \( \text{O}_2+\text{O}_2 \) system is proposed in Sec. II. In Sec. III A, the constructed StS kinetic database is presented. Then the rovibrational energy transfer and non-equilibrium dissociation are discussed in Sec. III B and Sec. III C respectively. Section III D provides the master equation results for the combined \( \text{O}_3 \) and \( \text{O}_4 \) systems. In Sec.
the present macroscopic results are compared with existing data from the literature. Finally, Sec. IV provides the conclusions from the present study.

II. PHYSICAL MODELING

A. Modeling of rovibrational energy transfer and dissociation of $O_2^{(X^3\Sigma_g^-)} + O_2^{(X^3\Sigma_g^-)}$ system

This work assumes that all species relevant to the $O_2 + O_2$ system remain in their electronic ground state during the collisional interaction. Then the rovibrational energy transfer and dissociation processes of the $O_2 + O_2$ system can be expressed as

\begin{align}
    O_2(i) + O_2(m) & \leftrightarrow O_2(j) + O_2(l), \quad (1) \\
    O_2(i) + O_2(m) & \leftrightarrow O + O + O_2(l), \quad (2) \\
    O_2(i) + O_2(m) & \leftrightarrow O_2(j) + O + O, \quad (3) \\
    O_2(i) + O_2(m) & \leftrightarrow O + O + O + O, \quad (4)
\end{align}

where the indices $(i, m, j, l)$ denote the rovibrational states of $O_2^{(X^3\Sigma_g^-)}$ that are stored by increasing energy in the set $I_{O_2}$. Each rovibrational level corresponds to a unique vibrational $(v)$ and rotational $(J)$ quantum number (e.g., $i = i(v, J)$). The reaction in Eq. (1) includes both the inelastic and exchange kinetics. The processes in Eqs. (2)-(4) contain dissociation from the direct and exchanged pairs. In the present master equation study, the double-dissociation reaction in Eq. (4) is neglected since it was found to have little influence for the conditions of present interest. Then the system of master equations describing the evolution of the rovibrational states of $O_2$ and the concentration of $O$ atom reads:

\[
\frac{dn_i}{dt} = \sum_j \sum_l \sum_m (-k_{im \rightarrow j} n_i n_m + k_{jl \rightarrow im} n_j n_l) + \sum_l \sum_m (-k_{im \rightarrow cl} n_i n_m + k_{cl \rightarrow im} n_0^2 n_l) + \sum_j \sum_m (-k_{im \rightarrow jc} n_i n_m + k_{jc \rightarrow im} n_j n_0^2),
\]

where $I_{O_2}$ is the set of rovibrational states of $O_2$.
\[ \frac{dn_O}{dt} = 2 \sum_i \sum_l \sum_m (k_{im \rightarrow c} n_i n_m - k_{cl \rightarrow im} n_O^2 n_l) + 2 \sum_i \sum_j \sum_m (k_{im \rightarrow cl} n_i n_m - k_{jc \rightarrow im} n_j n_O^2). \]

Here \( n_X \) identifies the number density of \( X \) species/level, and \( t \) denotes time. The rate coefficient \( k \) describes the corresponding bound-bound (e.g., \( k_{im \rightarrow jl} \)) and bound-free (e.g., \( k_{im \rightarrow cl} \)) transitions where the subscript \( c \) denotes the dissociated state. It is important to note that the rate coefficient \( k \) is a dependent variable of the kinetic temperature \( T \), although its dependency is omitted for brevity.

The description of the rovibrational energy transfer and dissociation of \( O_2 \) using Eqs. (5) and (6) requires a prohibitive amount of computational cost since \( O_2 (X^3\Sigma_g^-) \) has 6115 different rovibrational levels (see Sec. II B) resulting in about \( 6115^4 \) collisional processes to be considered. This constraint in the computational cost motivated the development of coarse-graining strategies. However, those order reduction strategies provide an approximated description of the StS population dynamics, rather than the complete rovibrational-specific distributions which are crucial ingredients in developing advanced reduced order models. This work thus presents a novel and simple reduced order model, which allows investigating the rovibrational distribution in the \( O_2 + O_2 \) system by combining the concept of coarse-grain QCT method with the model proposed by Kim et al. assumes a Boltzmann distribution among the collision partner’s internal states.

Derivation of the proposed model can start from Eqs. (1)-(4). We enforced the rovibrational states \( m \) of the collision partner being populated as a Boltzmann distribution at a prescribed internal temperature \( T_{\text{int}} \) by introducing a state-specific distribution function \( F_m \):

\[ F_m (T_{\text{int}}) = \frac{n_m}{n_{O_2}} = \frac{Q_m (T_{\text{int}})}{Q_{O_2} (T_{\text{int}})}. \]

The partition functions \( Q_m \) and \( Q_{O_2} \) are defined as

\[ Q_m (T_{\text{int}}) = g_m \exp \left( -\frac{e_m}{k_B T_{\text{int}}} \right), \quad Q_{O_2} (T_{\text{int}}) = \sum_m Q_m (T_{\text{int}}), \]

where \( e_m \) and \( k_B \) denote the \( m \)-th state energy and the Boltzmann constant, respectively. The rovibrational degeneracy \( g_m = g_{\text{nuc}} (2J + 1) \) includes the nuclear spin contribution as \( g_{\text{nuc}} = 0.5 \) for all the levels based on a semiclassical approximation. Then Eqs. (1)-(4) can
be recast as:

\[ O_2(i) + O_2(T_{\text{int}}) \leftrightarrow O_2(j) + \sum_l O_2(l), \]  
\[ O_2(i) + O_2(T_{\text{int}}) \leftrightarrow O + O + \sum_l O_2(l), \]  
\[ O_2(i) + O_2(T_{\text{int}}) \leftrightarrow O_2(j) + O + O, \]  
\[ O_2(i) + O_2(T_{\text{int}}) \leftrightarrow O + O + O + O, \]  

where \( O_2(T_{\text{int}}) \) denotes the collision partner Boltzmann-populated at \( T_{\text{int}} \). It is important to note that Figure C1 in the Supplementary Material verifies the insignificant impact of the double-dissociation in Eq. (12) by comparing the thermal dissociation rate coefficients from the mechanisms in Eqs. (10)-(12). By neglecting the double-dissociation, the set of master equations corresponding to Eqs. (9)-(11) leads to:

\[
\frac{dn_i}{dt} = \sum_j \left( -k_{i\rightarrow j}(T_{\text{int}}) n_i n_{O_2} + k_{j\rightarrow i}(T_{\text{int}}) n_j n_{O_2} \right)
\]
\[
- k_{i\rightarrow c}(T_{\text{int}}) n_i n_{O_2} + k_{c\rightarrow i}(T_{\text{int}}) n_O^2 n_{O_2}
\]
\[
+ \sum_j \left( -k^{*}_{i\rightarrow j}(T_{\text{int}}) n_i n_{O_2} + k^{*}_{j\rightarrow i}(T_{\text{int}}) n_j n_O^2 \right),
\]  

\[
\frac{dn_O}{dt} = 2 \sum_i \left( k_{i\rightarrow c}(T_{\text{int}}) n_i n_{O_2} - k_{c\rightarrow i}(T_{\text{int}}) n_O^2 n_{O_2} \right)
\]
\[
+ 2 \sum_i \sum_j \left( k^{*}_{i\rightarrow j}(T_{\text{int}}) n_i n_{O_2} - k^{*}_{j\rightarrow i}(T_{\text{int}}) n_j n_O^2 \right).
\]  

The form of rate coefficients \( k_{i\rightarrow j}, k_{i\rightarrow c}, \) and \( k^{*}_{i\rightarrow j} \) can be defined as

\[
k_{i\rightarrow j}(T_{\text{int}}) = \sum_l \sum_m k_{im\rightarrow jl} F_m(T_{\text{int}}),
\]
\[
k_{i\rightarrow c}(T_{\text{int}}) = \sum_l \sum_m k_{im\rightarrow cl} F_m(T_{\text{int}}),
\]
\[
k^{*}_{i\rightarrow j}(T_{\text{int}}) = \sum_m k_{im\rightarrow jlc} F_m(T_{\text{int}}),
\]

where \( k_{i\rightarrow j}, k_{i\rightarrow c}, \) and \( k^{*}_{i\rightarrow j} \) correspond to the reactions in Eqs. (9), (10), and (11), respectively. It is important to note that dependency of the rate coefficients to collision partner’s initial and final states (i.e., \( m \) and \( l \)) is eliminated by prescribing their internal distributions. This implies that the computational cost for \( O_2 \left( X^3\Sigma_g^- \right) + O_2 \left( X^3\Sigma_g^- \right) \) system for the given
and $T$ can be reduced to the same order of the one for $O_2 \left( X^3 \Sigma_g^- \right) + O \left( ^3P_2 \right)$. Consequently, solutions from Eqs. (13) and (14) describe the rovibrational energy transfer and dissociation in $O_2 \left( X^3 \Sigma_g^- \right) + O \left( X^3 \Sigma_g^- \right)$ system with much less computational expense compared with the exact formulation in Eqs. (5) and (6). The aforementioned order reduction strategy can be interpreted as a coarse-grain QCT model: The target species is fully-resolved to its rovibrational states, whereas the collision partner is grouped as a single bin in which all the levels are lumped into.

The rovibrational-specific state-to-state rate coefficients in Eqs. (15)-(17) are computed by means of the QCT method discussed in Sec. II B. At a given $T$, the QCT calculations are carried out for several $T_{\text{int}}$ that range from 300 K to $T$ (See Table I for more details). To integrate the set of master equations in Eqs. (13) and (14), the rate coefficients $k$ and $k^*$ depending on the $T_{\text{int}}$ are updated at each time step by interpolating them in $T_{\text{int}}$-space. This strategy is adopted to perform the master equation study at $T=10\,000$ K, whereas for other $T$ the rate coefficients are averaged over $T_{\text{int}}$-space and kept as constant values for further reduction of computational costs. It is important to note that the latter averaging approach does not affect to the key findings of the present work. The aforementioned reduced-order modeling strategy is denoted as thermal collider (TC) approach in the following sections.

The integration of the master equations is carried out using plato (PLAsms in Thermodynamic nOn-equilibrium), a library for non-equilibrium plasmas developed within The Center for Hypersonics and Entry System Studies (CHESS) at University of Illinois at Urbana-Champaign. In the master equation analysis to be presented, the chemical composition is initialized to have 100% of $O_2$. The initial gas pressure and internal temperature are set to 1000 Pa and 300 K, respectively. Those conditions are applied for all simulations unless otherwise stated. As per the heat-bath temperatures, the values of 7500 K, 10\,000 K, 15\,000 K, and 20\,000 K are considered.

B. Quasi-classical trajectory calculations

To compute the rovibrational-specific StS rate coefficients for Eqs. (9)-(12), QCT calculations are performed using COARSEAIR. It is an in-house QCT code that is a modernized version of the original VVTC code developed at NASA Ames Research Center by Schwenke. The three different ab-initio PESs proposed by Paukku et al. are employed
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to consider the adiabatic interactions occurring in the electronic ground state of $O_2+O_2$ system through the singlet, triplet, and quintet spin couplings. The statistical weights for each spin interaction are approximated as 1/9, 3/9, and 5/9, respectively, based on the high-temperature limit. The 6115 rovibrational energy levels are obtained by solving Schrödinger’s equation based on the WKB semi-classical approximation\cite{27,28}. Resultant dissociation energy of the rovibrational ground state is found as 5.113 eV. The initial state of thermal collision partner $O_2 (T_{int})$ is sampled from the prescribed distribution function $F_m (T_{int})$. Consequently, the rate coefficients in Eqs. (15)-(17) are computed by summing up the statistics of individual trajectories with respect to the final state of collision partner.

For a given bound-bound transition, both endothermic and exothermic trajectories can exist as the result of QCT calculations. In this case, one of them must be selected as a reference direction and the other one needs to be reconstructed based on the micro-reversibility to guarantee appropriate equilibration of the initial heat-bath simulations. In the present QCT calculations, the sampled trajectories are investigated to decide which direction (i.e., endothermic or exothermic) has better statistics as presented in Sec. A where detailed discussion is provided. As a result, we utilize the endothermic sampled trajectories as the reference forward direction with higher priority than the exothermic ones to construct the StS kinetic database described in Sec. III A. Exceptionally, the exothermic trajectory is used in a case that the given reaction channel does not have the endothermic one. The reverse rate coefficients are then reconstructed based on the micro-reversibility.

III. RESULTS

A. State-to-state kinetic database

The constructed StS kinetic database in this work covers the kinetic temperature range 7500-20 000 K. The combination of $T$ and $T_{int}$ for the QCT calculations are summarized in Table I. The present analysis at $T=10 000$ K ensures the highest fidelity in terms of accuracy since it covers the largest number of QCT databases along the $T_{int}$-space. The results in this work at other $T$, such as 7500 K, 15 000 K, and 20 000 K demonstrate the extension of the present modeling strategy to various kinetic temperature range. This section investigates influences of the sampling temperature $T_{int}$ on the constructed StS kinetic database, espe-
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cially for the inelastic and target particle’s dissociation of Eqs. (15) and (16), respectively.

**TABLE I:** Covered kinetic and internal temperatures in the present StS kinetic database.

| $T$     | $T_{\text{int}}$            |
|---------|----------------------------|
| 7500 K  | 300 K, 3500 K, 7500 K      |
| 10 000 K| 300 K, 2500 K, 5000 K, 7500 K, 10 000 K |
| 15 000 K| 300 K, 15 000 K            |
| 20 000 K| 300 K, 20 000 K            |

Figure 1 shows the inelastic rate coefficient distributions at $T=10 000$ K. The magnitude of rates is overlayed on the diatomic potential of $O_2\left(X^3\Sigma_g^-ight)$. Overall trends observed from both $T_{\text{int}}$ are qualitatively similar to each other: In the low-lying states, transition pathways are mostly aligned to the same vibrational strands, whereas they are spread across different vibrational levels in the high-lying energy regime. This may imply that the assumption for separation between rotational and vibrational states are less feasible in the high-energy area. A distinct difference according to the variation of $T_{\text{int}}$ is the rate coefficient for vibrational ladders. At the higher $T_{\text{int}}$, the vibrational transition rates are larger particularly in the low-$v$ and low-$J$ region that governs majority of the rovibrational energy transfer. This difference is quantitatively highlighted in Fig. 2. The rotational transition shown in Fig. 2(a) is not sensitive to the variation of $T_{\text{int}}$. Magnitudes of the rotational transition rates are almost identical to each other. On the other hand, the vibrational excitation rates change more than an order of magnitude for the variation of $T_{\text{int}}$ as observed in Fig. 2(b). As $T_{\text{int}}$ increases, the vibrational energy transfer is significantly raised. This increase is started to saturate at $T_{\text{int}}=5000$ K. From the investigations in Figs. 1 and 2, it is found that the sampling temperature $T_{\text{int}}$ has significant influence on the vibrational transition rates, whereas the impact to the rotational transitions is insignificant.

The target particle’s dissociation rate coefficient distributions are presented in Fig. 3. The figure compares the rates calculated at the three-different $T_{\text{int}}$. The dependence of the rate coefficient is a function of the distance from the centrifugal barrier. This behavior was observed by Venturi et al. In the case of $T_{\text{int}}$ around 10 000 K, the rate coefficients for
Rotational quantum number, $J$ - Energy, eV

0 50 100 150 200
0 2 4 6 8

$T_{\text{int}}=300$ K

$O_2(v_{\text{max}}, J)$

$O_2(v=0, J)$

$\log_{10}(k_{i\to j}(T_{\text{int}}))$ [cm$^3$/s]

$T_{\text{int}}=10,000$ K

$O_2(v_{\text{max}}, J)$

$O_2(v=0, J)$

$\log_{10}(k_{i\to j}(T_{\text{int}}))$ [cm$^3$/s]

FIG. 1: Distributions of the inelastic rate coefficients in Eq. (9) at $T_{\text{int}}=300$ K (top) and $T_{\text{int}}=10,000$ K (bottom) at $T=10,000$ K, overlayed on the $O_2$ diatomic potential. The gray dots indicate that the internal states having the rate coefficients lower than a cutoff value of $k_{i\to j}(T_{\text{int}})=1.58\times10^{-12}$ cm$^3$/s. The black dots represent the initial target states.

$O_2+O_2$ are indistinguishable from the ones computed for the $O_2+O$ system (See Fig. C5).

Influence of the $T_{\text{int}}$ variation is confined to the low-lying energy levels which do not have a significant impact on the dissociation kinetics. By relating the rates with the concept of energy deficit, defined as a distance from the centrifugal barrier in energy space, it is clear that the $T_{\text{int}}$ of colliding molecule works as a stretching factor for the magnitude of rates, especially for the states far away from the centrifugal barrier. This is because as collision partner has higher internal energy (i.e., higher $T_{\text{int}}$), the low-lying states of target $O_2$ can more easily gain the required barrier energy to dissociate during collisions.

It is important to note that in the high-lying energy states the rates are very close to
FIG. 2: Distributions of the inelastic rate coefficients in Eq. (9) at $T=10{,}000\,$K. The initial target states are: (a) O$_2$(v=0, J=10) and (b) O$_2$(v=2, J=10).

each other and consequently a difference of the thermal rate coefficients between $T_{\text{int}}=300\,$K and $10{,}000\,$K is less than a factor of 1.5 at $T=10{,}000\,$K. Figure C6 supports this aspect by showing more quantitative distributions of the rates for some selected quantum pairs.

### B. Internal energy transfer processes

In this section, internal energy transfer by the inelastic and exchange kinetics is studied in detail by neglecting the dissociation mechanisms while solving the set of master equations. The influence of sampling temperature $T_{\text{int}}$ on the rovibrational population dynamics by the inelastic process is firstly investigated at $T=10{,}000\,$K. Then the master equation analysis is extended to other kinetic temperatures along with examination of the exchange process.

Figure 4 presents snapshots of the rovibrational distributions by the inelastic process at a time instant $t=10^{-7}\,$s and $T=10{,}000\,$K. The time instant $10^{-7}\,$s is selected to compare the distributions in the early stage of energy transfer. Overall structures at the different $T_{\text{int}}$ values are similar to each other. At the higher $T_{\text{int}}$, the excited vibrational levels are more populated that can be verified from the slope among the heads of vibrational strands which implies the vibrational temperature $T_V$. At the same time instant, the rate of average
vibrational energy transfer at $T_{\text{int}}=10000$ K occurs about 2 times faster compared to that in $T_{\text{int}}=300$ K.

The master equation study is extended to other kinetic temperatures to investigate global trend of rovibrational energy transfers in the O$_2$+O$_2$ system. Figure 5 shows the temporal evolution of vibrational ($T_V$) and rotational ($T_R$) temperatures along the variation of $T$. From the master equation results, the characteristic rotational-translational ($\tau_{RT}$) and vibrational-translational ($\tau_{VT}$) relaxation times are determined using the \textit{e-folding} method. Then they are fed into the linear Landau-Teller (L-T) relaxation equation to compare with the internal energy transfers from the master equation study. The L-T relaxation equation can be expressed as

$$\frac{dE_V}{dt} = \frac{E_{V,\text{eq}} - E_V}{\tau_{VT}},$$

(18)
FIG. 4: Rovibrational distributions at $T_{\text{int}}=300 \text{ K}$ (top) and $T_{\text{int}}=10000 \text{ K}$ (bottom) at $T=10000 \text{ K}$ by the inelastic kinetics only. The distributions are extracted from the identical time instant $t=10^{-7} \text{ s}$ and colored by the vibrational quantum number.

$$\frac{dE_R}{dt} = \frac{E_{R,eq} - E_R}{\tau_{RT}},$$

where $E_V$ and $E_R$ are the average energy of vibration and rotation, respectively. The subscript $eq$ indicates the quantity evaluated at the equilibrium temperature $T$. It is important to note that the L-T model reasonably reproduces the master equation results in the considered $T$ range as shown in the figure. Although the difference between the vibrational and rotational characteristic relaxation times is reduced as $T$ increases (See Fig. [16]), the rotational energy transfer is distinctly faster than the vibration in the considered temperature range.

The internal energy transfer processes in O$_2$+O$_2$ system are analyzed in detail by investigating time evolution of rovibrational distributions as shown in Fig. [6]. The figure presents the distributions at $T=10000 \text{ K}$. In the early times, the low-lying levels form several distinct vibrational strands whereas the high-lying states near the dissociation limit are preferentially excited than the others around (See $t=1e-08 \text{ s}$ and $t=1e-07 \text{ s}$) due to the exchange kinetics. The quasi-bound levels having higher energy than 6.5 eV are quickly equilibrated to each
FIG. 5: Temporal evolution of (a) vibrational and (b) rotational temperatures of O$_2$ at the different heat-bath temperatures (dissociation kinetics excluded). The solid lines are obtained from the master equation analysis while the symbols are computed based on the Landau-Teller relaxation model.

other that forms a Boltzmann distribution in the tail region. From $t=1e-08$ s to $t=1e-07$ s, the excitation of high-lying states is saturated and thermalization among the low-lying levels is slowly followed. One of important findings of the present study is that in O$_2$+O$_2$ system the thermalization among different vibrational levels is relatively slower than that of O$_2$+O. This finding is attributed to the two facts: In O$_2$+O$_2$, (1) the inelastic process occurs in more rotation-favorable ways rather than the vibration, and (2) the exchange kinetics is much less effective in comparison with those of O$_2$+O. The aforementioned points are discussed in detail through Figs. 7-9.

Figure 7 highlights the influence of exchange kinetics on the internal energy transfer of the O$_2$+O$_2$ and O$_2$+O systems. The lower and upper bounds of $T$ are considered. Results obtained from a present VS model for the O$_2$+O$_2$ system are also presented as comparison group. The rovibrational-specific kinetic database for the O$_2$+O system used in the present study is taken from the work by Venturi et al. Obviously, the exchange kinetics has little impact on the internal energy transfer of the O$_2$+O$_2$ system, whereas it significantly hastens the relaxation of O$_2$+O. This fact results in the different rate of thermalization among the
FIG. 6: Rovibrational distributions along $t$ at $T=10000\,\text{K}$ (dissociation kinetics excluded). The dashed vertical line indicates the average dissociation energy of $\text{O}_2$, 5.113 eV.

internal energy states. In $\text{O}_2+\text{O}_2$, the equilibration among different vibrational strands slowly occurs as observed from Fig. 6. On the contrary, the exchange process advances the mixing of the internal levels in $\text{O}_2+\text{O}$ system. Figure C7 presents more details of it in terms of the rovibrational distributions of $\text{O}_2+\text{O}$. The exchange reaction more favorably occurs in $\text{O}_2+\text{O}$ compared to the $\text{O}_2+\text{O}_2$, since the 3-atom system has lower effective barrier for bond breaking required for the particle exchange.

Figure 8 provides an alternative interpretation regarding the results shown in Fig. 7 on a more microscopic scale. The figure compares the rovibrational distributions in the $\text{O}_2+\text{O}_2$ and $\text{O}_2+\text{O}$ systems at $T=10\,000\,\text{K}$. Both distributions are extracted from the 20% of vibrational relaxation to make the direct comparison. The two systems commonly have the strand-like structures in the low-lying energy regime. In the $\text{O}_2+\text{O}_2$, impact of the exchange process is only confined to levels near the dissociation limit that can be inferred by comparing Figs. 4 and 8(top). On the other hand, in $\text{O}_2+\text{O}$ most of the vibrational strands are already thermalized, except for some low-lying levels having the state energy less than 1.5 eV. The result in Fig. 8 implies that fundamental structure of the rovibrational distributions between the two systems is different to each other. It is important to note that the difference observed from Fig. 8 is not only from the exchange kinetics but also attributed to the inelastic process.
FIG. 7: Influence of exchange kinetics on the internal energy transfer. (a) $\text{O}_2+\text{O}_2$ with the TC model, (b) $\text{O}_2+\text{O}_2$ with the VS model, and (c) $\text{O}_2+\text{O}$ with the fully-StS approach. The dissociation kinetics is excluded.

Even though with the inelastic kinetics only, the rovibrational distributions of $\text{O}_2+\text{O}_2$ are more broadly spread than those of $\text{O}_2+\text{O}$, especially in the low-lying energy region in which the energy transfer is dominated by the inelastic kinetics.

The different natures in the inelastic kinetics can be more effectively distinguished by investigating the vibrational transition probability $P(v_i \rightarrow v_j)$ due to the inelastic where $v_i$
FIG. 8: Rovibrational distributions in $\text{O}_2+\text{O}_2$ (top) and $\text{O}_2+\text{O}$ (bottom) systems at 20% of vibrational relaxation at $T=10\,000\,\text{K}$ (dissociation kinetics excluded). The distributions are colored by the vibrational quantum number.

and $v_j$ are the initial and final vibrational quantum numbers of the target $\text{O}_2$. Figure 9 shows the distributions of $P(v_i\rightarrow v_j)$ in $\text{O}_2+\text{O}_2$ and $\text{O}_2+\text{O}$ systems at $T=10\,000\,\text{K}$. The probability is computed by summing up the individual probabilities, which are obtained from the QCT calculations, along with the initial and final rotational states. In $\text{O}_2+\text{O}_2$, the $P(v_i\rightarrow v_j)$ distribution is more clustered around the diagonal line (i.e., $v_i=v_j$) compared to $\text{O}_2+\text{O}$, implying that the vibrational transition is less favorable. In the same vein, distributions of the rotational transition probability $P(J_i\rightarrow J_j)$ are also provided to Fig. C8, confirming that the $\text{O}_2+\text{O}$ system has more diagonally-clustered probability, resulting in the faster rate of vibrational transitions through the inelastic process.

C. Dissociation/recombination processes

In this section, dissociation and recombination processes in $\text{O}_2+\text{O}_2$ system are investigated. Figure 10 shows temporal evolution of the internal temperatures and $\text{O}_2$ mole fraction along the variation of $T$. In the considered $T$ range, the plateau region of the temperatures
that implies the quasi-steady-state (QSS) period is clearly observed as shown in Fig. 10(a). In the QSS region, the rotational and vibrational temperatures are distinctly separated from each other, especially at $T=15,000\,\text{K}$ and $20,000\,\text{K}$. The slow thermalization among the vibrational strands discussed in Fig. 8 contributes to that separation by allowing that the two energy modes have certainly different gradients of population distributions (See Fig. C9 for more details). As shown in Fig. 10(b), it is confirmed that $\text{O}_2$ is completely dissociated in the given $T$ range. It is important to note that in Eq. (11) influence of combined inelastic and dissociation process is negligible, whereas combined exchange and dissociation kinetics has substantial contributions. This is because when exchange occurs in $\text{O}_2+\text{O}_2$ collision bond breaking happens that ends up the higher probability of the dissociation. In Fig. C10, the $\text{O}_2$ composition profiles by the TC model are compared with the VS approach. This demonstrates that the two methods represent reasonable agreement along the considered $T$ range.

Accuracy of the present modeling strategy for $\text{O}_2+\text{O}_2$ dissociation can be verified by comparing QSS vibrational populations with the existing result obtained from the DMS by
The normalized cumulative vibrational population $f_v$ is defined as

$$f_v = \sum_{J=0}^{J_{\text{max}}(v)} \frac{n_i(v, J)}{n_{O_2}},$$

where $J_{\text{max}}(v)$ implies the maximum rotational quantum number at the given $v$. It is important to note that comparison of $f_v$ can function as one of necessary conditions, but not as a sufficient one\cite{4, 31}.

Figure 11 shows the comparison of $f_v$ at QSS of $T=10\,000\,K$. The distributions are computed from the three different models. In the QSS region, the low-lying vibrational levels form a Boltzmann distribution whereas the high-lying ones are in strong non-Boltzmann state. The dissociation process is mostly governed by the high energy levels that confirms the $O_2+O_2$ dissociation occurs in a non-equilibrium manner during the QSS period. As shown in the figure, the results from the different models are in reasonable agreement that demonstrate the capability of the present TC approach to predict the QSS vibrational distribution of the molecule.

The rovibrational distribution at the molecular QSS period is one of the most important ingredients in studying physics behind dissociation kinetics. In this work, the QSS rovibrational distribution of $O_2+O_2$ is compared with that of $O_2+O$ as shown in Fig. 12 for
FIG. 11: Comparison of normalized vibrational distributions at QSS of $T=10\,000$ K.

$T=10\,000$ K. By comparing Figs. 12(a) and 12(b) it is found that structures of the distributions are different to each other; overall, $O_2+O_2$ system has a more scattered rovibrational population. This difference is mainly attributed to the dissimilarity in the behavior of energy transfers (i.e., inelastic and exchange), rather than the dissociation dynamics. As discussed in Sec. III B, $O_2+O_2$ system represents the significantly slower thermalization rate among the internal states, especially for the vibrational strands. This ends up the more scattered population distribution at the time the system enters the QSS period in which majority of $O_2$ molecule dissociates.

In Figs. 12(c) and 12(d) the QSS distributions are compared with those from the VS model. The rotational populations by the VS model are reconstructed by assuming the Boltzmann distribution at $T$. The comparisons are made in the middle of QSS regions, determined by the TC model in $O_2+O_2$ and by the Fully-StS approach in $O_2+O$, respectively. The inset figures present normalized $O_2$ mole fractions where $\chi_{O_2,0}$ implies the initial value of $\chi_{O_2}$. In $O_2+O_2$, the QSS distributions are well matched for the bound levels, whereas substantial discrepancy exists for the quasi-bound states. The VS model overestimates the quasi-bound populations. Albeit that difference, both models predict almost identical mole fraction profiles. In $O_2+O$, the mole fraction evolution calculated by the VS model is distinctly different from the Fully-StS approach: The VS model overestimates the amount of
dissociation. In the previous study by Venturi et al\textsuperscript{2}, the similar issue was addressed and an improved coarse-grain model for the O\textsubscript{2}+O dissociation kinetics was designed by leveraging the physics behind the diatomic potential and the centrifugal barrier. Since the faster thermalization quickly squeezes the rovibrational distribution, the high-lying levels around the dissociation limit have relatively larger contributions to the amount of dissociation in O\textsubscript{2}+O, compared with O\textsubscript{2}+O\textsubscript{2} in which the equilibration among the vibrational states is much slower in nature.

In Fig. 13 normalized rovibrational energy loss ratio $\epsilon_i/\epsilon_1$ is compared between O\textsubscript{2}+O\textsubscript{2} and O\textsubscript{2}+O systems. The state-specific internal energy loss ratio $\epsilon_i$ is calculated using the definition proposed by Panesi et al\textsuperscript{1} where $\epsilon_1$ is accumulated quantity of $\epsilon_i$ over the entire internal states. By using the present TC model for the O\textsubscript{2}+O\textsubscript{2} system, the $\epsilon_i$ can only be defined for the dissociation process in Eq. (10). This fact is one of the drawbacks of the present TC approach. In O\textsubscript{2}+O\textsubscript{2}, the distribution has more gradual shape, whereas it shows a spike-like structure in O\textsubscript{2}+O centered around the dissociation limit. From the comparison, it is found that in O\textsubscript{2}+O\textsubscript{2} the quasi-bound states have much less contribution to the dissociation-energy coupling than that of O\textsubscript{2}+O. This is attributed to the lower amount of rovibrational populations of the quasi-bound levels in O\textsubscript{2}+O\textsubscript{2} as discussed in Fig. 12.

D. Application to combined O\textsubscript{3}+O\textsubscript{4} system

In this section, the master equation analysis is extended to complete oxygen mixture that includes both O\textsubscript{2}+O\textsubscript{2} and O\textsubscript{2}+O interactions. Purpose of this extension is to investigate relative contributions from those two collisional systems to the internal energy transfer and dissociation of O\textsubscript{2} in the full oxygen mixture. The set of master equations corresponding to the combined O\textsubscript{3}+O\textsubscript{4} system is presented in App. B. The present results are compared with those of existing study by Grover et al\textsuperscript{6} obtained from the DMS method. For this comparison, the chemical components are initialized to have 100% of O\textsubscript{2} and initial number density of $2.414\times10^{19}$ cm\textsuperscript{-3}. The initial rotational and vibrational temperatures are set to 1394.3 K and 985.1 K, respectively. Then the kinetic temperature $T$ is suddenly raised to 10000 K and kept constant to study the non-equilibrium energy transfer and dissociation processes.

Figure 14 presents normalized average internal energy and O\textsubscript{2} mole fraction profiles. It is
FIG. 12: QSS rovibrational distributions of $\text{O}_2+\text{O}_2$ and $\text{O}_2+\text{O}$ systems at $T=10,000$ K. (a) and (b): The distributions are colored by the vibrational quantum number. (c) and (d): Comparison with the VS model. The inset figures indicate normalized $\text{O}_2$ mole fraction $\chi_{\text{O}_2}/\chi_{\text{O}_2,0}$.

important to note that for the present results shown in the figure the recombination process is turned off for consistency with the DMS result by Grover et al. Among the results, Present-Rovib implies a rovibrational-specific approach that is a hybrid of the TC model for $\text{O}_2+\text{O}_2$ and the Fully-StS method for $\text{O}_2+\text{O}$. For both average vibrational energy and $\text{O}_2$ mole fraction profiles, the present result by the rovibrational-specific approach represents better
agreement than the VS model compared to the reference DMS data. This improvement on the accuracy is mostly attributed to the rovibrational-specific treatment of the $O_2+O$ rather than $O_2+O_2$, since we observed that the VS and the TC approaches provide very similar macroscopic mole fraction profiles as shown in Fig. 12(c). The present average rotational energy profile shows a larger discrepancy from the DMS result than the vibration during the non-equilibrium energy transfer. According to the previous studies by Venturi et al. and Macdonald et al., it was demonstrated that the StS master equation approach yields very similar results with those from the DMS provided that the identical PES is adopted. Therefore, the discrepancy of the average rotational energy profile in Fig. 14(a) requires further investigation.

To the authors’ best knowledge, no detailed rovibrational distribution has been presented for the complete oxygen system. In Fig. 15, the evolution of rovibrational distributions and the time-cumulative dissociation production rate are presented. It should be noted that the recombination is now turned on to simulate the results shown in Fig. 15. Figure 15(a) confirms that the $O_2+O_2$ collision governs the early stage of energy transfer, since the rovibrational distribution at 10% of vibrational relaxation represents very similar structure with that of isolated $O_2+O_2$ shown in Fig. 8. At the QSS however, the $O_2+O$ collision
FIG. 14: Temporal evolution of (a) normalized average energy and (b) O₂ mole fraction. Comparison with the previous result by Grover et al.\textsuperscript{6}.

takes control of the oxygen mixture. This can be inferred from the fact that the QSS distribution shown in Fig. 15(a) is almost identical with that of isolated O₂+O shown in Fig. 12(b). One more important takeaway from Fig. 15(a) is the QSS distribution of the complete oxygen system (i.e., bottom) is clearly correlated with the each rovibrational level’s energy deficit $e_i^D$. This implies that the coarse-grain strategy\textsuperscript{22}, which was developed for the diatomic dissociation by correlating the energy deficit with the multi-group maximum entropy approach\textsuperscript{33}, can also be applied to the complete oxygen mixture case.

The quantity presented in Fig. 15(b) is defined by summing up and normalizing the mass production rate for the dissociation and recombination in Eq. (13) at given time-step with the total amount of chemical production rate relevant to dissociation and recombination. This definition was taken from the previous study by Jo et al.\textsuperscript{3} From the figure, it is found that before the onset of QSS most of the dissociation is dominated by O₂+O₂ collision. During the QSS period, about 35% of dissociation occurs in which O₂+O system has larger contribution than O₂+O₂. This observation is in line with the rovibrational distribution in Fig. 15(a). It is important to note that in total O₂+O₂ collision has larger contribution to the cumulative dissociation production rate. This is because the 4-atom system has more various dissociation pathways compared to the 3-atom system.
FIG. 15: (a) Rovibrational distributions in $\text{O}_3+\text{O}_4$ system at 10% of vibrational relaxation (top, colored by $v$) and QSS (bottom, colored by $e^D_i$). (b) Time-cumulative dissociation production rate. The cyan-shaded region indicates the QSS period of $\text{O}_2$. 
E. Comparison of characteristic quantity against existing data

In this section, the macroscopic quantities such as rovibrational relaxation time, dissociation rate coefficients, and average energy loss ratio obtained from the present analyses are compared with existing data.

Figure 16 compares the rotational and vibrational relaxation times of O$_2$+O$_2$ system with data in the literature $^{6,7,11,34-38}$. The symbol $p$ implies the pressure of collision partner. The present vibrational relaxation time by the TC model is in good agreement with the DMS data $^6$. The result from the VS approach however shows the distinctly shorter relaxation time at $T=15,000$ K and $20,000$ K, and represents closer agreement with the Park model including high-temperature correction $^{37}$. In comparison with the measured data $^{7,11,34}$, the present TC result has slightly improved agreement than the VS model. It is worth mentioning that the $p\tau_{VT}$ data measured from the recent experiments $^{7,11}$ represents longer relaxation time than the present results. The rotational relaxation time $p\tau_{RT}$ by the present TC model shows significant discrepancy compared to the Parker model $^{35}$, which was derived by classical mechanics along using the rigid-rotor approximation. From the present result by the TC model, it is found that in O$_2$+O$_2$ collision the convergence of the rotational and vibrational relaxation time to a common asymptote in high-temperature range $^{39}$ is relatively weak in comparison to other 3-atom systems, such as N$_2$+N $^{40}$, O$_2$+O $^{41}$, N$_2$+O and NO+N $^{42}$.

Figure 17 compares the present QSS dissociation rate coefficients in O$_2$+O$_2$ system with data from literature $^{6,7,11,37,42-45}$. Since some of excited electronic states of O$_2$ are closely spaced near the ground level, the multi-surface correction factor $^{46} 16/3$ is multiplied to the present QSS rate coefficients to consider the dissociating contribution from the excited electronic states. Those results are labeled as $w$ Corr. Fac. in the figure. The present results from the TC and VS models are in very close agreement to each other, and they are well matched with the DMS data $^6$. In case that the multi-surface correction factor is considered, the predicted data by this work shows better agreement with the measurements $^{7,12,45}$, except for the non-equilibrium experiment by Ibraguimova et al. $^{11}$. This measured data is closer to the present result that does not include the correction factor. The trend of inconsistency implies the uncertainty of both measurement and modeling to consider dissociation from the excited electronic states. It is worth mentioning that the Park model $^{37}$ represents somewhat different temperature dependency compared to the present data in the high-temperature
FIG. 16: Comparison of predicted rotational and vibrational relaxation times in O$_2$+O$_2$ system with existing experimental and theoretical data.

region. In Fig. C12 the overall QSS dissociation rates predicted by the TC model shown in Fig. 17 are decomposed into the individual component by the two reaction channels in Eqs. (10) and (11).

In Fig. 18 comparison of the average energy loss ratio for the combined oxygen mixture (i.e., O$_3$+O$_4$) is presented. It is important to note that unlike in Fig. 17 the multi-surface correction factor here is multiplied to the rovibrational-specific dissociation rate coefficients to consider the nonlinear nature in the master equations (See Eq. (13)). In Fig. 18(a), the predicted results are compared with the measured vibrational energy loss ratio by Streicher et al. The present rovibrational-specific result shows closer agreement with the measured data than the VS approach which overpredicts the measured quantity. Including the multi-surface correction factor improves the agreement between the experimental data and the present rovibrational-specific calculations by lowering the predicted value. This fact implies that the contribution of the excited electronic states to the dissociation is commonly captured by both the experiment and the numerical modeling. It is found that the average rotational energy loss ratio is relatively less sensitive to the multi-surface correction, especially at $T=7500$ K and 10 000 K. This might be attributed to the fact that the dissociation is mostly controlled by the high-$v$ and low-$J$ levels at those temperatures. Then as $T$ increases, the
FIG. 17: Comparison of predicted QSS dissociation rate coefficients in O₂+O₂ system with existing experimental data and theoretical predictions.

high-J levels at low-v region have larger contribution that ends up the greater sensitivity to the multi-surface correction. It should be noted that the QSS value of the average energy loss ratio of the combined O₃+O₄ is almost identical with that of O₃ (i.e., O₂+O) only. It is because the dissociation of O₃+O₄ during the QSS period is mostly governed by the O₃ as observed from Fig. 15. This fact is supported by Fig. 18(b) showing the decomposition of the average vibrational energy loss ratio. During the QSS period, the overall curve in red is very close to that of O₃. From the present investigation, we concluded that the measured quantity by Streicher et al. [1] is most likely regarding the O₂+O collision rather than O₂+O₂.

IV. CONCLUSIONS

This work proposes a reduced-order rovibrational kinetic model of the O₂+O₂ system for applications relevant to high-enthalpy flows. To overcome the exponential number of possible reactive channels that characterizes the diatom-diatom systems, the population of internal levels of one of the reactants is assumed to follow a Boltzmann distribution at a prescribed internal temperature. Detailed QCT calculations are performed to determine
The rovibrational-specific kinetic database constructed covers a wide temperature range (7500-20 000 K) and is used in the master equation solver to study the kinetics of thermo-chemical relaxation in isothermal isochoric conditions. To the author’s best knowledge, this work constitutes the first application of the rovibrational master equation approach to a diatom-diatom system (except for the H₂+H₂ system, which is far more straightforward). The results obtained have been compared with the DMS calculations showing excellent agreement in the population distribution and averaged energy and composition.

The main findings are summarized below:

• The rovibrational population distribution of the O₂ molecules is found to depart from equilibrium throughout the dissociation process. The extent of non-equilibrium is more pronounced if compared to the O₂+O case. Furthermore, the vibrational-rotational mixing is less efficient than in the O₂+O case leading to a more distinct separation of the rotational strands characterized by a constant vibrational quantum number. The strands exhibit significant curvature due to the less efficient inelastic and exchange
energy processes.

- The internal temperature used to prescribe the population of the collision partner has an impact on the results. It leads to a parametrization of the reaction rate parameters in the function of $T$ and $T_{\text{int}}$.

- The analysis of the combined $O_3+O_4$ system shows how $O_2+O_2$ collision governs the energy transfer in the early stage, while $O_2+O$ takes control of the dissociation physics in correspondence to the QSS period. This is an important finding as it facilitates the construction of reduced-order models for oxygen chemistry.

- Finally, the predicted macroscopic quantities, such as the rovibrational relaxation times, QSS dissociation rate coefficients, and dissociation-vibration coupling constants, agree with the available literature data. This fact provides validity to the physical model devised in the present work.

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Appendix A: Characteristics of sampled trajectories at $T_{\text{int}}$

In Fig. A1(a), the number of sampled bound-bound trajectories are presented at $T=10\,000\,\text{K}$ and $T_{\text{int}}=300\,\text{K}$. A bound-bound trajectory denotes that a given initial collision pair ends up to another one in which both target and collider are in the bound or quasi-bound states. For each energy level, 30,000 trajectories are simulated. Majority of the trajectories lead to bound final states for the low-lying initial target level (i.e., low level index $i$). As the initial target state is aligned to higher $v$ and $J$, the final energy level is more probable to end up in the dissociated state.

Figure A1(b) shows the sampled bound-bound trajectories decomposed into the endothermic and exothermic forward directions. Determination of the energy direction is done using the individual trajectories that are not summed up for the collision partner’s final state. As a result, all of the four energy levels in Eq. (1) are considered. In the sampled trajectories, the endothermic direction overwhelms the exothermic one, especially in the low-lying energy levels that govern the rovibrational energy transfer. This also happens for the trajectory calculations at $T_{\text{int}}=10\,000\,\text{K}$ as shown in Fig. C2 in the Supplementary Material. The fact observed from Fig. A1 implies that the endothermic transitions of the low-lying states are more probable to occur in description of the rovibrational-translational (RV-T) and RV-RV energy transfers when the initial states of collision partner are sampled from the Boltzmann distribution at a given $T_{\text{int}}$.

In a similar vein, Fig. C3 shows ratio of the number of sampled trajectories by Eq. (9) to the exact one from Eq. (1) for both exothermic and endothermic directions. It is clear that the endothermic trajectories has better sampling quality than those of the exothermic direction, especially for the heads of each $v$ (i.e., $i=i(v, J=0)$) that governs the vibrational energy transfer.
FIG. A1: Number of sampled bound-bound trajectories at \(T=10,000\,\text{K}\) and \(T_{\text{int}}=300\,\text{K}\). (a) Total and (b) decomposition into endothermic and exothermic trajectories. The distributions are colored by the vibrational quantum number.

Appendix B: Master equations for combined \(\text{O}_3+\text{O}_4\) system

The set of master equations corresponding to the combined \(\text{O}_3+\text{O}_4\) system leads to:

\[
\frac{dn_i}{dt} = \sum_j \left( \sum_{T_{\text{int}}} \left( -k_{i\rightarrow j} (T_{\text{int}}) n_i n_{\text{O}_2} + k_{j\rightarrow i} (T_{\text{int}}) n_j n_{\text{O}_2} - k_{i\rightarrow c} (T_{\text{int}}) n_i n_{\text{O}_2} + k_{c\rightarrow i} (T_{\text{int}}) n_j^2 n_{\text{O}_2} + \sum_{T_{\text{int}}} \left( -k_{i\rightarrow j} (T_{\text{int}}) n_i n_{\text{O}_2} + k_{j\rightarrow i} (T_{\text{int}}) n_j n_{\text{O}_2} + \sum_{T_{\text{int}}} \left( -\tilde{k}_{i\rightarrow j} n_i n_{\text{O}} + \tilde{k}_{j\rightarrow i} n_j n_{\text{O}} \right) - \tilde{k}_{i\rightarrow c} n_i n_{\text{O}} + \tilde{k}_{c\rightarrow i} n_{\text{O}}^3 \right) \right) \right),
\]

\[
\frac{dn_{\text{O}}}{dt} = 2 \sum_i \left( k_{i\rightarrow c} (T_{\text{int}}) n_i n_{\text{O}_2} - k_{c\rightarrow i} (T_{\text{int}}) n_{\text{O}}^2 n_{\text{O}_2} \right) + 2 \sum_i \sum_j \left( k_{i\rightarrow j}^* (T_{\text{int}}) n_i n_{\text{O}_2} - k_{j\rightarrow i}^* (T_{\text{int}}) n_j n_{\text{O}}^2 \right) + 2 \sum_i \left( \tilde{k}_{i\rightarrow c} n_i n_{\text{O}} - \tilde{k}_{c\rightarrow i} n_{\text{O}}^3 \right),
\]

where \(\tilde{k}_{i\rightarrow j}, \tilde{k}_{j\rightarrow i}, \tilde{k}_{i\rightarrow c},\) and \(\tilde{k}_{c\rightarrow i}\) are the excitation/de-excitation and dissociation/recombination rate coefficients of \(\text{O}_2+\text{O}\) system.
Appendix C: Supplementary Material

**FIG. C1:** Distributions of thermal dissociation rate coefficients for $\text{O}_2+\text{O}_2$ system.
FIG. C2: Number of sampled bound-bound trajectories at $T=10\,000$ K and $T_{\text{int}}=10\,000$ K. (a) Total and (b) decomposition into endothermic and exothermic trajectories. The distributions are colored by the vibrational quantum number.
**FIG. C3:** Ratio of sampled bound-bound trajectories by Eq. (9) to Eq. (1) at $T=10\,000\,\text{K}$ and $T_{\text{int}}=300\,\text{K}$. (a) Exothermic and (b) endothermic trajectories. The distributions are colored by the vibrational quantum number. The value in $y$-ordinate indicates the number of trajectories that are misinterpreted in deciding the forward direction by relying on the sampling approach in Eq. (9). As this quantity is closer to one, the quality of the sampled trajectories is more reliable. It should be noted that, by introducing the sampling strategy, large number of trajectories are misinterpreted as the exothermic one that is actually in the reverse direction as shown in Fig. 3(a).
FIG. C4: Distributions of the dissociation rate coefficients in Eq. (16) at $T=10000$ K. (a) $T_{\text{int}}=10000$ K colored by the vibrational quantum number, (b) $T_{\text{int}}=300$ K, 7500 K, and 10000 K.

FIG. C5: Comparison between the dissociation rate coefficients of $O_2+O_2$ in Eq. (16) and that of $O_2+O \rightarrow 3O$ at $T=10000$ K.
FIG. C6: Distributions of the dissociation rate coefficients in Eq. (10) at $T=10000$K. The initial target states are: (a) $O_2(v=0, J)$, (b) $O_2(v=20, J)$, (c) $O_2(v=35, J)$. 
FIG. C7: Influence of the exchange kinetics on the rovibrational distributions of O_2+O system at $t=2.95 \times 10^{-8}$ s of $T=10000$ K in which 8.8% of vibrational relaxation occurs in case that the exchange process is considered. The initial mole fraction was set to $\chi_{O_2}=\chi_O=0.5$ and the dissociation process was excluded.

FIG. C8: Rotational transition probability distributions due to the inelastic process for (a) O_2+O_2 at $T_{\text{int}}=300$ K and (b) O_2+O at $T=10000$ K.
FIG. C9: Rovibrational distributions at QSS of $T=20,000$ K. The black arrows depict the gradients of rotational and vibrational distributions that imply their characteristic temperatures.

FIG. C10: Comparison of mole fraction profiles of O$_2$ between the TC and VS models.
FIG. C11: Comparison of the rovibrational distributions of $\text{O}_2+\text{O}$ system between the fully-StS and VS models at $T=10\,000$ K. The distributions are extracted at $\chi_{\text{O}_2}/\chi_{\text{O}_2,0}=0.2$.

FIG. C12: Distributions of QSS dissociation rate coefficients for $\text{O}_2+\text{O}_2$ system.
REFERENCES

1. M. Panesi, R. L. Jaffe, D. W. Schwenke, and T. E. Magin, “Rovibrational internal energy transfer and dissociation of $N_2(1\Sigma_g^+) - N(4\Sigma_u)$ system in hypersonic flows,” Journal of Chemical Physics 138, 044312 (2013).

2. S. Venturi, M. P. Sharma, B. Lopez, and M. Panesi, “Data-inspired and physics-driven model reduction for dissociation: Application to the $O_2 + O$ system,” Journal of Physical Chemistry A 124, 8359–8372 (2020).

3. S. M. Jo, S. Venturi, M. P. Sharma, A. Munafò, and M. Panesi, “Rovibrational-specific qct and master equation study on $N_2(X^1\sigma_g^+)+O(3p)$ and NO($X^2\pi$)+N($4s$) systems in high-energy collisions,” The Journal of Physical Chemistry A (2022), 10.1021/acs.jpca.1c10346.

4. M. S. Priyadarshini, S. M. Jo, S. Venturi, D. W. Schwenke, R. L. Jaffe, and M. Panesi, “Comprehensive study of HCN: Potential energy surfaces, state-to-state kinetics, and master equation analysis,” The Journal of Physical Chemistry A 0, null (0), pMID: 36288431.

5. S. M. Jo, A. Munafò, M. S. Priyadarshini, S. Venturi, and M. Panesi, “Rovibrational-specific master equation analysis of high-temperature air mixture,” in AIAA SCITECH 2022 Forum, https://arc.aiaa.org/doi/pdf/10.2514/6.2022-0342.

6. M. S. Grover, E. Torres, and T. E. Schwartzentruber, “Direct molecular simulation of internal energy relaxation and dissociation in oxygen,” Physics of Fluids 31, 076107 (2019).

7. J. W. Streicher, A. Krish, and R. K. Hanson, “Coupled vibration-dissociation time-histories and rate measurements in shock-heated, nondilute $O_2$ and $O_2$-Ar mixtures from 6000 to 14000 K,” Physics of Fluids 33, 056107 (2021).

8. E. Torres, E. C. Geistfeld, and T. E. Schwartzentruber, “Direct molecular simulation of rovibrational relaxation and chemical reactions in air mixtures,” in AIAA SCITECH 2022 Forum, https://arc.aiaa.org/doi/pdf/10.2514/6.2022-1010.

9. D. A. Andrienko and I. D. Boyd, “Vibrational energy transfer and dissociation in $O_2$–$N_2$ collisions at hyperthermal temperatures,” The Journal of Chemical Physics 148, 084309 (2018) https://doi.org/10.1063/1.5007069.

10. R. L. Macdonald, R. L. Jaffe, D. W. Schwenke, and M. Panesi, “Construction of a coarse-grain quasi-classical trajectory method. I. Theory and application to $N_2$–$N_2$ system,” Journal of Chemical Physics 148, 054309 (2018).
11. L. B. Ibraguimova, A. L. Sergievskaya, V. Y. Levashov, O. P. Shatalov, Y. V. Tunik, and I. E. Zabelinskii, “Investigation of oxygen dissociation and vibrational relaxation at temperatures 4000–10 800 k,” *Journal of Chemical Physics* **139**, 034317 (2013).

12. M. Lino da Silva, J. Loureiro, and V. Guerra, “A multiquantum dataset for vibrational excitation and dissociation in high-temperature O2–O2 collisions,” *Chemical Physics Letters* **531**, 28–33 (2012).

13. D. A. Andrienko and I. D. Boyd, “State-specific dissociation in O2–O2 collisions by quasiclassical trajectory method,” *Chemical Physics* **491**, 74–81 (2017).

14. A. J. C. Varandas and A. A. C. C. Pais, “Double many-body expansion potential energy surface for O4(3A), dynamics of the O(3P) + O3(1A1) reaction, and second virial coefficients of molecular oxygen,” in *Theoretical and Computational Models for Organic Chemistry*, edited by S. J. Formosinho, I. G. Csizmadia, and L. G. Arnaut (Springer, Dordrecht, 1991) pp. 55–78.

15. Y. Paukku, K. R. Yang, Z. Varga, G. Song, J. D. Bender, and D. G. Truhlar, “Potential energy surfaces of quintet and singlet O4,” *Journal of Chemical Physics* **147**, 034301 (2017).

16. Y. Paukku, Z. Varga, and D. G. Truhlar, “Potential energy surface of triplet O4,” *Journal of Chemical Physics* **148**, 124314 (2018).

17. S. M. Jo, M. Panesi, and J. G. Kim, “Prediction of shock standoff distance with modified rotational relaxation time of air mixture,” *Physics of Fluids* **33**, 047102 (2021).

18. A. Sahai, B. Lopez, C. O. Johnston, and M. Panesi, “Adaptive coarse graining method for energy transfer and dissociation kinetics of polyatomic species,” *Journal of Chemical Physics* **147**, 054107 (2017).

19. J. G. Kim and I. D. Boyd, “State-resolved thermochemical nonequilibrium analysis of hydrogen mixture flows,” *Physics of Fluids* **24**, 086102 (2012).

20. J. G. Kim, O. J. Kwon, and C. Park, “Master equation study and nonequilibrium chemical reactions for hydrogen molecule,” *Journal of Thermophysics and Heat Transfer* **24**, 281–290 (2010).

21. V. T. Baluckram and D. Andrienko, “First-principle simulation of vibrational activation and dissociation in oxygen shock flows,” in *AIAA Scitech 2021 Forum*.

22. A. Munafò, M. Panesi, R. L. Jaffe, G. Colonna, A. Bourdon, and T. E. Magin, “QCT-based vibrational collisional models applied to nonequilibrium nozzle flows,” *European Physical Journal D* **66**, 188 (2012).
Jo et al.

23. M. P. Sharma, Y. Liu, and M. Panesi, “Coarse-grained modeling of thermochemical nonequilibrium using the multigroup maximum entropy quadratic formulation,” *Physical Review E* **101**, 013307 (2020).

24. A. Sahai, C. O. Johnston, B. Lopez, and M. Panesi, “Flow-radiation coupling in CO$_2$ hypersonic wakes using reduced-order non-boltzmann models,” *Physical Review Fluids* **4**, 093401 (2019).

25. A. Munafò, A. Alberti, C. Pantano, J. B. Freund, and M. Panesi, “A computational model for nanosecond pulse laser-plasma interactions,” *Journal of Computational Physics* **406**, 109190 (2020).

26. S. Venturi, R. L. Jaffe, and M. Panesi, “Bayesian machine learning approach to the quantification of uncertainties on ab initio potential energy surfaces,” *Journal of Physical Chemistry A* **124**, 5129–5146 (2020).

27. D. W. Schwenke, “Calculations of rate constants for three-body recombination of H$_2$ in the presence of H$_2$,” *Journal of Chemical Physics* **89**, 2076–2091 (1988).

28. D. G. Truhlar and J. T. Muckerman, “Reactive Scattering Cross Sections III: Quasiclassical and Semiclassical Methods,” in *Atom-molecule Collision Theory. A Guide for the Experimentalist*, edited by R. B. Bernstein (Springer US, 1979) pp. 505–566.

29. C. Park, *Nonequilibrium Hypersonic Aerothermodynamics* (Wiley, New York, NY, 1990).

30. L. Landau and E. Teller, “Theory of sound dispersion,” Phys. Z Sowjetunion **10**, 34–43 (1936), in German.

31. R. L. Macdonald, M. S. Grover, T. E. Schwartzentruber, and M. Panesi, “Construction of a coarse-grain quasi-classical trajectory method. II. Comparison against the direct molecular simulation method,” *Journal of Chemical Physics* **148**, 054310 (2018).

32. R. L. Macdonald, E. Torres, T. E. Schwartzentruber, and M. Panesi, “State-to-state master equation and direct molecular simulation study of energy transfer and dissociation for the N$_2$-N system,” *Journal of Physical Chemistry A* **124**, 6986–7000 (2020).

33. Y. Liu, M. Panesi, A. Sahai, and M. Vinokur, “General multi-group macroscopic modeling for thermo-chemical non-equilibrium gas mixtures,” *Journal of Chemical Physics* **142**, 134109 (2015).

34. S. A. Losev and N. A. Generalov, “A study of the excitation of vibrations and dissociation of oxygen molecules at high temperatures,” in *Soviet Physics Doklady*, Vol. 6 (1962) p. 1081.
35. J. G. Parker, “Rotational and vibrational relaxation in diatomic gases,” *Physics of Fluids* **2**, 449–462 (1959).

36. R. C. Millikan and D. R. White, “Systematics of vibrational relaxation,” *Journal of Chemical Physics* **39**, 3209–3214 (1963).

37. C. Park, “Review of chemical-kinetic problems of future NASA missions, I: Earth entries,” *Journal of Thermophysics and Heat Transfer* **7**, 385–398 (1993).

38. J. G. Kim, S. H. Kang, and S. H. Park, “Thermochemical nonequilibrium modeling of oxygen in hypersonic air flows,” *International Journal of Heat and Mass Transfer* **148**, 119059 (2020).

39. J. G. Kim and S. M. Jo, “Modification of chemical-kinetic parameters for 11-air species in re-entry flows,” *International Journal of Heat and Mass Transfer* **169**, 120950 (2021).

40. J. G. Kim and I. D. Boyd, “State-resolved master equation analysis of thermochemical nonequilibrium of nitrogen,” *Chemical Physics* **415**, 237–246 (2013).

41. S. Venturi, M. Sharma Priyadarshini, A. Racca, and M. Panesi, “Effects of ab-initio potential energy surfaces on O₂-O non-equilibrium kinetics,” in *AIAA Aviation 2019 Forum*.

42. C. J. Schexnayder and J. S. Evans, “Measurements of the dissociation rate of molecular oxygen,” NASA TR-R-108 (1961).

43. M. Camac and A. Vaughan, “O₂ dissociation rates O₂-Ar mixtures,” *Journal of Chemical Physics* **34**, 460–470 (1961).

44. O. Shatalov, “Molecular dissociation of oxygen in the absence of vibrational equilibrium,” *Combustion, Explosion and Shock Waves* **9**, 610–613 (1973).

45. J. W. Streicher, A. Krish, S. Wang, D. F. Davidson, and R. K. Hanson, “Measurements of oxygen vibrational relaxation and dissociation using ultraviolet laser absorption in shock tube experiments,” in *AIAA Scitech 2019 Forum*.

46. E. Nikitin, M. Kearsley, and O. U. Press, *Theory of Elementary Atomic and Molecular Processes in Gases* (Clarendon Press, 1974).