Simulation of Oxygen Dissociation on a Six-dimensional \( \text{O}_4 \) Potential Energy Surface

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The quasi-classical trajectory method is applied to obtain the state-resolved dissociation rate coefficients of oxygen in collisions with another oxygen molecule. A six-dimensional potential energy surface, constructed using the double many-body expansion method is used. The results of simulation suggest that the \( \text{O}_2–\text{O}_2 \) rate coefficients can not be obtained by a scaling of a simpler \( \text{O}_2–\text{O} \) dataset, nor by applying the preferential dissociation model with a constant adjustable parameter. Depletion via an exchange mechanism significantly contributes to the total dissociation rate coefficient at temperatures below 5000K and at low vibrational energies. The new dataset of rate coefficients is used in a zero-dimensional heat bath simulation.

I. Introduction

The development and application state-resolved (SR) models of thermally nonequilibrium flows is a topic of increasing interest in aerothermochemistry. Resolving transitions between individual energy levels of species instead of assuming the Boltzmann population of these energy levels at some internal temperature is an important advantages of SR models over the conventional multi-temperature (MT) models. A large number of datasets aiming to fill the gap in state-specific RCs of air species was generated over the last decade due to ever-growing computational capabilities. Most of the studies are dedicated to three-body collisions, i.e. when a molecule (typically, either \( \text{O}_2 \) or \( \text{N}_2 \)) collides with an atom. The SR simulation of molecule-molecule system is conducted less often due to either the absence of an adequate potential energy surface (PES) or due to the large cost of resolving all transitions between internal states arising in four-body collisions. Moreover, oxygen chemistry is studied less often compared to nitrogen, mainly because oxygen quickly dissociates during a flight of reentry vehicle. However, oxygen thermal relaxation and dissociation can be important for the design of hypersonic vehicles that travel at moderate hypersonic Mach numbers.

The SR simulation of oxygen shock flows is complicated by the presence of \( \text{O}_2–\text{O}_2 \) collisions that are dominant immediately behind the shock front due to the absence of atomic species. An accurate SR model would require a six-dimensional \( \text{O}_4 \) PES that accounts for the bond breaking mechanism. To the authors knowledge, a global \textit{ab-initio} \( \text{O}_4 \) PES is yet to be proposed. The only \( \text{O}_4 \) PES that can adequately describe dissociation was developed by.\(^1\) For this reason, the present paper concentrates on the \( \text{O}_2–\text{O}_2 \) state-resolved dissociative collisions using the Varandas PES.

The structure of the paper is as follows. Section II provides a discussion about the \( \text{O}_4 \) PES and four-body QCT simulations. Section III compares the QCT dissociation RC with the available theoretical and experimental data. Section IV presents the study of state-specific coefficients obtained in the \( \text{O}_4 \) QCT simulation. Conclusions are reported in Section VI.

II. \( \text{O}_4 \) potential energy surface and trajectory propagation

Previous studies of vibrational energy transfer in \( \text{O}_2–\text{O}_2 \) collisions were mostly concentrated on low temperatures that are of relevance for ozone formation in the upper atmosphere.\(^1–4\) Billing and Coletti used...
a semi-empirical PES that does not include bond breaking mechanisms. For this reason, the investigation in\(^4\) is limited to temperatures up to 1000 K. In two former works, a six-dimensional double many-body expansion (DMBE I) PES is used, and is adopted in the present work. The DMBE I PES by Varandas is triplet and is designed to explain the “shadow” mechanism of ozone extinction:

\[
O \left( ^3P \right) + O_3 \left( ^1A_1 \right) \rightarrow 2O_2 \left( X^3\Sigma_g^- \right)
\]  

(1)

Later, the DMBE I PES was revised by\(^5\) in order to eliminate the spectator bond mechanism,\(^6\) originally observed in trajectory simulations on the DMBE I PES. In the DMBE II PES, an extra four-body energy term of the extended Hartree-Fock type was added. This alleviates the probability of one oxygen molecule to emerge from the reaction with higher internal energy than the other O\(_2\) molecule. However, as stated by,\(^7\) this correction introduces a spurious minimum in the DMBE II PES which is yet to be eliminated. For this reason, the present work implements the original DMBE I PES.

The following reaction of state specific dissociation of oxygen is studied:

\[
O_2 \left( v \right) + O_2 \rightarrow 2O + O_2,
\]  

(2)

where the vibrational state of the first diatom is fixed while the vibrational state of the second diatom is sampled at some vibrational temperature \(T_v\) according to the Boltzmann distribution. Following this procedure, a SR dissociation rate coefficient (RC) of oxygen in vibrational state \(v\) is obtained. The quasiclassical trajectory (QCT) method is used to accumulate sufficient statistics of reaction (2). The details of the four-body QCT method are described elsewhere.\(^7\)

The present in-house QCT code is capable of handling three- and four-body collisions (see\(^8\) and references therein). For molecule-molecule simulations, the QCT code generates cross sections for nine possible channels: bound-bound inelastic channel, direct dissociation of target or projectile, double exchange of atoms, exchange with a subsequent dissociation of target or projectile, formation of a triatomic molecule, double dissociation and elastic collision. For the study of the SR target depletion, channels of direct dissociation and dissociation via exchange are important. The double dissociation channel contributes negligibly in the range of temperatures between 3000 and 15,000 K.

The DMBE I PES supports the formation of the triatomic molecule, i.e. ozone in a ground vibrational state. In the present work, O\(_3\) formation is observed as well, however such trajectories are not counted toward the dissociation channel. In fact, capturing of such trajectories with short memory about initial state presents a computational challenge. The present study integrates trajectories for a sufficiently long time to ensure that formation of ozone is captured accurately.

The potential energy curve of diatomic oxygen generates 46 excited vibrational levels and a maximum of 234 rotational levels for the O\(_2\) ground electronic state. The vibrational energies and turning points of each rovibrational state are calculated by the Wentzel-Kramers-Brillouin method. The total number of rovibrational levels in the ground electronic state of oxygen is 6,213, however, even numbered rotational states are not taken into account to follow the selection rules of nuclear spin statistics. In all QCT calculations, the rotational states of both target and projectile are sampled according to the Boltzmann distribution at \(T_r=T\), where \(T_r\) and \(T\) are the rotational and translational temperatures, respectively.

A database of bound-free RCs in the range of temperatures between 3000 and 15,000 K is generated. In theory, these rate coefficients should be modified to take into account two factors: A) the degeneracy of reactants and PES and B) the contribution of electronic states in the depletion mechanism. Ideally, these factors should be obtained from the trajectory branching via the QCT method that accommodates all possible PES that arise in O\(_2\) (X)–O\(_2\) (X) collisions and their intersections.\(^9\) However, not only are such PESs unavailable, but also the branching in the QCT method would be prohibitively more expensive than the standard QCT method. Taking into account that the Varandas O\(_3\) PES was derived using semi-empirical assumptions, the implementation of empirically derived corrections factors seems to be the most reasonable choice.

Since the O\(_3\) PES describes the lowest energetic configuration of the O\(_3\)+O \(\rightarrow\) 2O\(_2\) reaction, it is reasonable to assume that only 1/3 of reactions that lead to bound-bound transitions occur on this PES. Previously, a similar factor of 1/27 was applied for the O\(_2\)-O system when the QCT method was implemented on the O\(_3\)\(^{1}A_1\) PES.\(^10\) However, bound-free transitions can occur not only on the lowest PES. In fact, dissociation rate coefficients typically show a little sensitivity to PESs with different long range forces but with a similar short range repulsive wall. This was observed for O\(_2\)-N\(_2\)\(^{11}\) and for O\(_2\)-O\(_2\)\(^{12}\) collisions. Moreover, an \textit{ab-initio} study of O\(_2\)-O\(_2\) spin-spin interaction by\(^3\) has revealed insignificant differences in a repulsive wall
between dimers in singlet, triplet and quintet states. Thus, the current approach assumes that dissociation RCs of reaction (2) on the DMBE PES are similar to those on PESs of other degeneracy and, hence, no modification is needed, despite the fact that O\textsubscript{2}–O\textsubscript{2} is 9-fold degenerate in the ground electronic state and the multiplicity of the DMBE PES is only 3.

Meanwhile, the dissociation of molecular oxygen in shock waves with a temperature above a few thousands degrees is unlikely to proceed in an adiabatic manner. One way to account for alternative channels of dissociation from excited electronic states is to assume an equilibrium between lower vibrational levels of an excited electronic state and high vibrational levels of the ground state.\textsuperscript{13} The contribution of dissociation from excited electronic states should be added to the dissociation RC from the ground electronic state. This assumption leads to the factor of 16/3, originally proposed by Nikitin for O\textsubscript{2} dissociation. This factor provides an excellent agreement between the QCT method and experimental data for O\textsubscript{2}–O dissociation.\textsuperscript{14} As will be shown later, the implementation of such a factor in O\textsubscript{2}–O\textsubscript{2} dissociation RCs would lead to a strong overestimation of the experimental data. One of the reasons for this is due the fact that electronic excitation in O\textsubscript{2}–O\textsubscript{2} collisions can be less efficient than in O\textsubscript{2}–O collisions. This statement is based on intuition of strong attraction in the barrierless O\textsubscript{3} PES, when the projectile particle can closely approach the target, which results in the efficient "scrambling" of internal energy, and erases the memory of reactants about their initial state. The present O\textsubscript{3} PES is less reactive than the DMBE O\textsubscript{3} PES and, hence, the electronic excitation may not be that efficient. In fact, the global dissociation rate coefficient obtained via the DMBE I O\textsubscript{4} PES without additional modification for electronic excitation is closely described by the experimental RC.

Comparison of one-dimensional cuts of the O\textsubscript{4} PES is shown in Fig. 1 for the low intermolecular energies and in Fig. 2 for energies relevant to the present study. The long-range forces create attraction between two oxygen molecules. Both PESs developed by Aquilanti et al. and by Coletti and Billing are similar in the depth and the slope of the potential well. For some collisional configurations, such as X and H, the PES by Aquilanti is less attractive, and for other configurations the agreement between the Aquilanti and Coletti PESs is very good. The PES by Varandas is different from both other PESs for all considered collisional configurations. The former PES is less repulsive, and for X and H configurations the attractive part of the potential is non-monotonic.

The comparison of the repulsive part, shown in Fig. 2, is given only for the Varandas and Coletti PESs. In this case, large discrepancies are also observed. For all collisional configurations, Varandas PES is significantly more repulsive than the Coletti PES. These differences are an order of several eV at a fixed intermolecular distance. This is expected, since the Coletti PES includes only a pairwise exponential term given by short-range forces and does not include a four-body term, unlike the Varandas PES. The remaining differences between the considered PESs make an additional, possibly \textit{ab-initio}, development of an O\textsubscript{4} potential highly desirable.

### III. Results

#### A. Thermal equilibrium dissociation RC

One of the possible ways to validate the present dataset is to compare the QCT dissociation RC with the available experimental data. Usually, the thermally equilibrium RC, \(D^{EQ}\), is reported in the literature, i.e. the dissociation rate that is observed when the population of the vibrational ladder corresponds to the Boltzmann distribution at given \(T_v = T\). In order to obtain \(D^{EQ}\), both vibrational states of reactants in Eq. (2) are sampled according to the Boltzmann distribution in the range of temperatures between 3000 and 15,000 K. For a realistic modeling of nonequilibrium flows, such a RC should be used together with a nonequilibrium dissociation model.

However, in shock tube measurements, a nonequilibrium dissociation RC, that corresponds to the non-Boltzmann population of the vibrational ladder, is actually measured. Often, this nonequilibrium dissociation RC is referred to as the quasi steady state (QSS) RC, \(D^{QSS}\), since the most intense chemical transformations occur after the incubation period when the vibrational energy of the gas reaches a plateau. During the QSS phase, the gain of vibrational energy via the interaction of vibrational and translational modes is approximately equal to the loss of internal energy due to depletion. The effective dissociation RC is nearly constant, and it is smaller than \(D^{EQ}\) due to the underpopulation of excited vibrational states. This was demonstrated via the state-resolved simulations of N\textsubscript{2}–N and O\textsubscript{2}–O collisions using a high fidelity set of RCs.\textsuperscript{14,15}
Fig. 1. Comparison of one-dimensional PES cuts using the data from Varandas et al.,\textsuperscript{1} Aquilanti et al.,\textsuperscript{3} and Coletti et al.\textsuperscript{4}
It is possible to establish a relation between $D^{EQ}$ and $D^{QSS}$ using the Fokker-Planck equation for the diffusion component of the distribution function. After some manipulations, the following expression is obtained:

$$D^{QSS}(T,T_v) = D^{EQ}(T,T_v) \frac{T}{T_v} \exp \left( \frac{E_{D^*}}{k_B} \left( \frac{1}{T} - \frac{1}{T_v} \right) \right),$$

where $E_{D^*}$ is the average loss of vibrational energy during dissociation: $E_{D^*} = E_D - \beta k_B T$, $\beta$ is between 1 and 2. Some uncertainty in Eq. (3) is related to how the vibrational temperature $T_v$ depends on $T$. In the experimental work by, the dependence of $T_v$ on $T$ was derived using numerical solution of the two-temperature vibrational energy conservation equation along with the experimental measurements. In the present work, results shown by curve 1 in Fig. 2 in are taken to model the dependence of $T_v$ on $T$. Additionally, $\beta$ is set to 2.

The present $O_2$–$O_2$ thermally equilibrium RC is shown in Fig. 3 by the solid line. For comparison, $O_2$–$O$ $D^{EQ}$, obtained on a $O_2$ DMBE PES, is shown by the dashed line. The experimental data is shown by empty circles. The equilibrium $O_2$–$O_2$ $D^{EQ}$, derived from shock tube measurements, is shown by filled diamonds. Note, that the experimental data, shown in Figs. 3 was processed using Eq. (3).

The QCT $O_2$–$O_2$ $D^{EQ}$ agrees well with the experimental data for temperatures below 5000 K, and it is at the upper boundary of experimental data at $T>5000$ K. There is also very good agreement between the previously recommended RC and the present data. As expected, dissociation in $O_2$–$O$ collisions at the equilibrium population of the vibrational ladder at $T_v = T$ occurs nearly three times faster than in $O_2$–$O_2$ collisions.

The QCT dissociation RCs, shown in Fig. 3, were not modified for electronic excitation. In this case, good agreement is observed for temperatures below 7000 K. Being multiplied by a factor of 16/3, as was done for $O_2$–$O$, the present RC will strongly overestimate the experimental data. A possible explanation lies in the fact that the electronic excitation in $O_2$–$O_2$ collisions may be less efficient than in $O_2$–$O$, for which a factor of 16/3 was originally proposed. The effect of the additional four-body term, introduced in the MBE II PES, may contribute at these energies. Of course, there is also a possibility that the DMBE I PES is too reactive. In this case, an ab-initio study of the $O_4$ complex is highly desired.

In the future, when state-resolved bound-bound transition RCs become available, one can obtain the QS dissociation RC from master equation simulations, which allows a more direct comparison with the experimental data. From the experimental point of view, this can be attributed to the difficulties in measuring the QSS dissociation RC, since the QSS assumption may not be valid under strong thermal nonequilibrium. This and other factors lead to a large scatter in the experimental data, sometimes up to an order of magnitude. Nevertheless, satisfactory agreement between the QCT data and experimental measurements makes the state-resolved simulations of oxygen dissociation feasible. The present QCT data, shown in Fig. 3, can be curve fitted to the Arrhenius form:

$$D^{EQ} = 2.707 \times 10^{-3} T^{-1.319} \exp \left( -6305/T \right), \text{ cm}^3/\text{s}. \quad (4)$$

Using a set of state-specific dissociation RCs, it is possible to derive $D^{QSS}$, and perform a direct comparison with the experimental data and theoretical RCs recommended in the literature. A system of master equations, describing the population of individual vibrational states, is solved in a manner similar to $O_2$ relaxation in a heat bath of oxygen atoms. For $O_2$–$O_2$ relaxation, a set of vibration-translation and vibration-vibration RCs is generated using the FHO model with the parameter of repulsiveness $\alpha=4.0$ 1/Å. Only $O_2$–$O_2$ collisions are considered, and $O_2$–$O$ collisions are artificially excluded from simulations. A comparison of QSS RCs is shown in Fig. 4.
The QSS experimental data by Shatalov was calculated from the reported equilibrium values using Eq. (3). Diamond symbols correspond to the RC recommended in,\textsuperscript{19} calculated at governing temperature \( T_a = \sqrt{T_v} \), where \( T_v \) corresponds to the vibrational temperature during the QSS phase. Solid and dashed lines describe \( O_2-O_2 \) and \( O_2-O \) QSS dissociation RCs obtained on \( O_4 \) and \( O_3 \) PESs.

\[ D_{QSS} = 3.717 \times 10^{-5} T^{-1.027} \exp \left(-58540/T\right), \text{ cm}^3/\text{s}. \] \hspace{1cm} (5)

IV. State-resolved \( O_2(v)-O_2 \) dissociation rate coefficients

Because the four-body QCT calculations are computationally expensive, the dissociation RCs are obtained only for \( v=0, 10, 20, 30 \) and \( 35 \) vibrational states and additionally for the last seven vibrational states \( v=40 \) ... 46. Missing RCs are obtained via an interpolation procedure.

The variation of the QCT RCs with vibrational energy is shown in Fig. 5. The state-specific dissociation RC is a semi-log function of vibrational energy for all but the very highest lying states. Namely, the semi-log dependence is only valid for energies less than 4.5 eV \( (v < 35) \). At higher energies, the dissociation from the excited states occurs more rapidly. For this reason, the dissociation RCs for \( v = 40 \) ... 46 are obtained directly, rather than from the interpolation procedure.

In order to understand differences in the ratio of equilibrium and QSS dissociation RCs, the state-resolved QCT data is analyzed. Comparison of \( O_2(v)-O \) and \( O_2(v)-O_2 \) RCs, obtained on \( O_4 \) and \( O_3 \) PESs, is shown in Fig. 6 at temperatures of 3000 and 10,000 K. It follows immediately that \( O_2(v)-O \) state-resolved RCs can be obtained at lower cost from \( O_2(v)-O_2 \) by employing only a variable scaling factor, similarly to the approach in.\textsuperscript{20} Recently, a similar scaling procedure was developed for \( N_2-N \) and \( N_2-N_2 \) collisions.\textsuperscript{21}

At low temperatures, low-\( v \) bimolecular dissociation RCs are approximately twice larger than the \( O_2(v)-O \) dissociation RCs. Toward high vibrational states, \( O_2-O_2 \) dissociation RCs are smaller than the \( O_2-O \) RCs. At \( T=10,000 \) K, \( O_2(v)-O_2 \) RCs are smaller than \( O_2-O \) RCs for all vibrational states. Note that the dissociation RC increases linearly in semi-log coordinates over a wide range of vibrational energy with the exception of highly-excited vibrational states. For these states, the increase of \( D_i \) occurs in a much faster...
manner, compared to the rest of the ladder. This result is observed for both sets of QCT simulations on the O$_4$ and O$_3$ PES.

![Graphs showing variation of state-resolved dissociation rates and state-specific dissociation rates](image)

**Fig. 5.** Variation of the state-resolved dissociation rates obtained on the O$_4$ PES with vibrational energy O$_2$(v)–O$_2$ RCs at 3000 and 10,000 K

**Fig. 6.** State-specific dissociation O$_2$(v)–O and O$_2$(v)–O$_2$ RCs at 3000 and 10,000 K

The contribution of specific states to the QSS dissociation RCs can be directly accessed from the master equation simulation. The cumulative contribution of individual vibrational states to $D_{QSS}$ is shown in Fig. 7(a) for T=3000K and 10,000K and for O$_2$–O and O$_2$–O$_2$ collisions. For comparison, the contribution of individual vibrational states to the equilibrium dissociation RC is shown in Fig. 7(b).

At 3000 K, the cumulative curves for $D_{QSS}$ are similar to those for $D_{EQ}$. This is explained by the small degree of nonequilibrium during the QSS state at mild heat bath conditions. Low vibrational states contribute more to O$_2$–O$ D_{QSS}$, particularly due to higher state-specific RCs and, at the same time, due to slower vibrational relaxation. The situation is different at 10,000 K. Due to strong nonequilibrium effects at this temperature, lower vibrational states contribute more to $D_{QSS}$ compared to their contribution at 3000K. This observation together with the discussion of Fig. 6 explains the smaller ratio of QSS RCs for O$_2$–O and O$_2$–O$_2$ collisions in comparison with the ratio of equilibrium dissociation RCs. In other words, the differences in ratio of dissociation RCs is due to high state-specific RCs generated on the O$_4$ Varandas PES as well as by a faster vibrational relaxation in the O$_3$ complex compared to that in O$_4$ at the studied temperatures.

It is interesting to compare the QCT state-specific O$_2$–O$_2$ RCs with those available in the literature. Besides the empirical model of preferential dissociation, the FHO model can be used to generate state-specific RCs of vibrational-vibrational, vibrational-translational energy transfer as well as of dissociation. The latter was performed da Silva using the Morse potential with a repulsive parameter of 4.0 1/Å. The FHO model is a powerful tool and probably is one of the few alternatives to the QCT method when non-empirical RCs are desired. However, the FHO model does not take into account multiple channels of reaction that lead to thermodynamically indistinguishable products. In the case of O$_4$ simulations, it will be shown that both exchange and direct dissociation channels contribute significantly. At the same time, the effect of anharmonicity on the species composition can be significant as well, especially taking into account nonlinear increase of RCs for high-v states, shown in Fig. 5. The comparison of the FHO RCs with the present QCT dataset is given in Fig. 8(a) and 8(b) for low and high lying vibrational states. The contribution of exchange channel in the present QCT results is shown in Fig. 9.

For states with low vibrational energy, the QCT model provides RCs that are approximately 5 to 10 times higher than the FHO RCs. As vibrational energy increases, the differences between QCT and FHO models become small. The RCs for the last five vibrational states are plotted separately to emphasize the different temperature dependence of RCs. For the state located near the dissociation limit, the dissociation RC varies much slower than for states with low energy.

It follows that the exchange channel, when one of the atoms in a target molecule is replaced by an atom from the projectile diatom, and a newly formed target diatom dissociates, significantly affects properties...
of states with low vibrational energy in the entire range of studied temperatures. When both direct and exchange channels are taken into account, the QCT RC for \( v=0 \) is higher than the FHO RC by one to two orders of magnitude in the range between 3000 and 15,000 K. The QCT RCs, given by only the direct channel, show a better agreement with the FHO RCs compared to the total channel of reaction (2). The disagreement between the FHO and QCT models becomes smaller with the vibrational quantum number; and this can be partially attributed to the closure of the exchange channel.
V. Heating and cooling heat bath conditions

The newly generated state-specific rate coefficients are applied to the simulation of vibrationally cold and hot oxygen in a heat bath with a constant translational temperature. In these simulations, both O$_2$–O and O$_2$–O$_2$ collisions are included. The O$_2$–O vibrationally resolved bound-free and bound-bound RCs were obtained previously\textsuperscript{14} using the Varandas O$_3$ PES.\textsuperscript{25} This PES can be obtained from the present O$_4$ PES by removing one of the atoms. The rotational structure of the rate coefficients, reported in Ref.\textsuperscript{14} is averaged at a given translational temperature according to the Boltzmann distribution. For the O$_2$–O$_2$ bound-bound VT and VV rate coefficients, the FHO model\textsuperscript{23} is used with a repulsive parameter of 4 Å$^{-1}$. Two sets of O$_2$–O$_2$ bound-free transitions are used. The first one is obtained via the O$_4$ QCT simulations. The second set is obtained by the FHO model with parameters described in Ref.\textsuperscript{24} In other words, the simulation of the heat bath conditions is conducted with the O$_2$–O$_2$ dissociation dataset being the only varying parameter in a kinetic scheme.

First, a case of vibrationally cold gas is considered. The time evolution of vibrational temperature in a heat bath of 6000, 8000 and 10,000K and $T_0^v=100$K is shown in Fig. 10. Solid lines correspond to the solution obtained using the QCT dataset, the dashed lines describe the results of the FHO model. Initially, the flow contains only molecular oxygen with the number density of $10^{18}$ cm$^{-3}$. As follows from Fig. 8, at these translational temperatures the state-specific dissociation RCs, generated by the QCT model, are larger than those of the FHO model. Depletion of the O$_2$ vibrational ladder occurs more slowly when the FHO dataset is implemented, causing an increased vibrational temperature during the QSS phase, as can be seen in Fig. 10. Depletion of the vibrational ladder leads to the decrease of temperature during the QSS phase. The non-monotonic behavior of temperature is more pronounced at higher translational temperatures when the flow contains a significant amount of atomic oxygen, since the dissociation in O$_2$–O collisions is more effective than in O$_2$–O$_2$ collisions.

In strong shock flows, the influence of O$_2$–O dissociative collisions is clearly important at the initial stage of the QSS phase being an initial source of atomic species. In a cooling gas at moderate initial vibrational temperatures, the influence of molecule-molecule collisions can be even more pronounced, since the fraction of molecular species remains large throughout the entire process of relaxation. The present paper simulates a cooling flow with the following parameters: $T=1000$K, $T_0^v=2000$K and $T=2000$K, $T_0^v=3000$K. The initial fraction of atomic oxygen is set to the equilibrium value at $T=T_0^v$: at $T=1000$K, it is equal to $2.1\times10^{15}$ cm$^{-3}$, t $T=2000$K it is set to $2.7\times10^{17}$ cm$^{-3}$.

The QCT simulations of the state-specific dissociation RCs at low translational temperatures is a computational challenge. However, as follows from Fig. 5, there is a linear temperature dependence between the natural logarithm of a RC and the vibrational energy of a state, if the vibrational energy of this state is significantly below the dissociation limit. At the same time, the QCT simulation of excited vibrational states is less challenging when resolving the dissociation channel. For the present purposes, the QCT dissociation
Fig. 10. Vibrational temperature at the heat-bath conditions, $T=6000$, 8000, and 10000K, $T=1000$ and 2000K given by the FHO\textsuperscript{24} and the present QCT models.

Fig. 11. State-specific O$_2$–O$_2$ dissociation RCs at $T=1000$ and 2000K given by the FHO\textsuperscript{24} and the present QCT models.

RCs are obtained for selected states with $v \geq 20$ and the RCs of states with $v < 20$ are linearly extrapolated as described previously. The QCT and FHO O$_2$–O$_2$ dissociation RCs at $T=1000$ and 2000K are shown in Fig. 11 with the solid and dashed lines, respectively. The temperature dependence of the QCT RCs is similar to that at higher temperatures in Fig. 5. The FHO RCs for states with $e_v < 3.5$ eV are significantly smaller than the QCT RCs. The states with higher energy have a non-monotonic behavior for the FHO RCs, which can probably be considered as a deficiency of the FHO model.

The population of the vibrational ladder during thermalization is shown in Figs. 12 and 13 for the heat baths of 1000K and 2000K, respectively. Due to the low translational temperature, a preferential recombination to excited vibrational states takes place. The bound-bound energy exchange between these states is efficient due to the small spacing between vibrational levels. This explains the existence of the long-lived plateau. Due to the non-monotonic behavior of the O$_2$–O$_2$ FHO RCs, the population of states with $e_v \approx 4.5$ eV is significantly higher than that predicted by the QCT model. As a result, the plateau in the case of FHO model is densely populated, compared to the results of the QCT model. Differences between the QCT and FHO models for the heat bath with $T=2000$K are smaller, particularly because of the initial higher abundance of atomic oxygen at $T_0 = 3000$K.

The influence of the O$_2$–O$_2$ dissociation model on macroscopic parameters, such as the species number density, is shown in Fig. 14. The QCT model predicts much faster recombination in the mixture with low translational temperature, compared to the FHO model. The differences in the composition of mixture with the higher initial fraction of atomic oxygen are smaller, as expected. Because at simulated conditions the plateau does not perturb the population of the lowest vibrational states, the vibrational temperatures given by the FHO and QCT models in all cooling heat bath conditions are similar to each other. This example demonstrates that the chemical composition in gas flows with $T_v > T$ is defined not only by the vibrational temperature but also depends on the kinetics of the excited vibrational states.

VI. Conclusion

A set of state-specific dissociation rate coefficients for molecular oxygen is generated. For the first time in the literature, the O$_2$(v)–O$_2$ dissociation RCs are obtained via the QCT method on a six-dimensional O$_4$ PES. Heat bath conditions are simulated using a system of master equations coupled to the new set of rate coefficients. Thermal equilibrium and QSS O$_2$–O$_2$ dissociation RCs are in satisfactory agreement with shock tube data, slightly overestimating the median experimental value at temperatures between 4000 and 10,000 K. The present set of dissociation RCs shows significant differences from those RCs obtained either via the preferential dissociation model or by means of the FHO model. This indicates the necessity in the QCT calculations on a more accurate O$_4$ PES in future.
Fig. 12. Population of vibrational ladder in the cooling heat bath conditions: $T=1000\text{K}$, initial $T_v=2000\text{K}$

Fig. 13. Population of vibrational ladder at the cooling heat bath conditions: $T=2000\text{K}$, initial $T_v=3000\text{K}$
Trajectory simulations, described in the present paper, revealed several interesting findings about the dissociation mechanism in O₂–O₂ collisions. First, the exchange channel contributes significantly to state-specific RCs, particularly at low temperatures and for states with low vibrational energy. Second, the state-specific O₂–O₂ dissociation RCs cannot be obtained from O₂–O RCs using a constant scaling factor. In fact, RCs for low vibrational states are similar for O₄ and O₃ molecular systems, while the high-v states dissociate much faster in O₂–O collisions. These results should be viewed keeping in mind the accuracy of the DMBE method that was used to construct the O₃ and O₄ PESs.

Vibrational temperature during the QSS phase is sensitive to the O₂–O₂ state-resolved dissociation RCs. An implementation of the FHO and QCT models for a simulation of heat bath conditions indicates that the variation in vibrational temperature can be non-monotonic during the QSS phase if the energy removal in molecule-molecule collisions is slow. In a situation of a vibrationally hot gas in a cold heat bath, the formation of a long-lived plateau due to preferential recombination is observed. This process is also highly sensitive to the O₂–O₂ dissociation model.

VII. Acknowledgments

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References


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