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State-specific dissociation in O_2–O_2 collisions by quasiclassical trajectory method

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ABSTRACT

State-specific dissociation rate coefficients of oxygen in collisions with another oxygen molecule are obtained using the quasiclassical trajectory method on a six-dimensional potential energy surface at high temperatures characteristic of hypersonic flows. The present results indicate that O_2–O_2 rate coefficients can not be obtained by a simple scaling of a simpler O_2–O dataset. A difference is observed between the present rate coefficients and those obtained via the preferential dissociation and forced harmonic oscillator models. Depletion via an exchange mechanism significantly contributes to the total dissociation rate at low temperatures and at low vibrational energies. The new set of rate coefficients is used in a one-dimensional shock flow simulation. The computed vibrational temperature is then compared to data obtained by absorption spectroscopy in the Schumann-Runge bands. A better agreement with the experimental data is achieved at moderate levels of nonequilibrium when the new dataset is implemented.

1. 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 O_2 or 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 O_2–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 O_4 PES that accounts for the bond breaking mechanism. To the authors knowledge, a global *ab initio* O_4 PES is yet to be proposed. The only O_4 PES that can adequately describe dissociation was developed by Varandas and Pais [22]. For this reason, the present paper concentrates on the O_2–O_2 state-resolved dissociative collisions using the Varandas PES.

The structure of the paper is as follows. Section 2 provides a discussion about the O_4 PES and four-body QCT simulations. Section 3 compares the QCT dissociation RC with the available theoretical and experimental data. Section 4 presents the study of state-specific coefficients obtained in the O_4 QCT simulation. Conclusions and curve fit data are reported in Sections 5 and Appendix A, respectively.

2. O_4 potential energy surface and trajectory propagation

Previous studies of vibrational energy transfer in O_2–O_2 collisions were mostly concentrated on low temperatures that are of relevance for ozone formation in the upper atmosphere [22,5,4,6]. Billing and Coletti used a semi-empirical PES that does not include bond breaking mechanisms. For this reason, the investigation in [6] is limited to temperatures up to 1000 K. In two former works, a six-dimensional double many-body expansion

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(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:

$$O(^3P) + O_3(^1A_1) \rightarrow 2O_2\left(X^3\Sigma_g^-\right) \tag{1}$$

Later, the DMBE I PES was revised by Varandas and Llanio-Trujillo [21] in order to eliminate the spectator bond mechanism [13], 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 molecules to emerge from the reaction with higher internal energy than the other O_2 molecule. However, as stated by Varandas and Llanio-Trujillo [21], 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:

$$O_2(v) + O_2 \rightarrow 2O + O_2, \tag{2}$$

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 [18].

The present in–house QCT code is capable of handling three- and four-body collisions (see [2] 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 the excited (O_3^*) and stable (O_3) states [23]. In the present work, ozone formation is observed as well. Capturing of such trajectories with a short memory about the initial state presents a computational challenge since the O_3^* complex can live for a long time before the atomic and molecular species become separated from each other. The present study integrates trajectories for a sufficiently long time to ensure that the formation of ozone is captured accurately. As follows from Varandas and Wang [23], the duration of reactions leading to the O_3^* formation can be as long as hundreds of femtoseconds, while the mean free time at conditions studied in the present paper, is between 10^{-8} and 10^{-10} s. For this reason, reactions leading to the formation of excited ozone are counted toward the dissociation channel. On the contrary, reactions with the formation of stable ozone do not contribute to the dissociation channel. Rates of O_3 formation are compared to the dissociation rates in the results section.

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 take 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.

In the present work, the simulation of molecule–molecule collisions is conducted using an in–house four-body QCT code. An extensive overview of three- and four-body QCT methods is given elsewhere [18]. Collisions of particles are simulated at energies between 0.1 and 6 eV in order to obtain the converged RCs at high temperatures. The initial collisional energy is fixed in each batch, rather than being sampled randomly. This step increases the statistical uncertainty of results, however it fully retains the dependence of cross sections on collisional energy. For vibrational states with $v \geqslant 20$, the size of a batch varies between 2000 and 100 trajectories per each increment of impact parameter which is set to 0.1 Å. The QCT simulations of lower vibrational states at T = 3000 K are conducted in a slightly modified manner due to poor statistical accuracy of a traditional sampling technique. Namely, the energy balance of target and projectile particles is considered to avoid propagating trajectories with energy insufficient for dissociation of a target molecule. Quantitatively, the following condition must hold in order to make the dissociation of the target possible:

$$E_{kin} + E_{in}^{proj} \geqslant E_{diss}^{targ}, \tag{3}$$

where E_{kin} is the kinetic energy of particles separated by a sufficiently large distance, E_{in}^{proj} is the internal energy of a projectile, E_{diss}^{targ} is the energy required to dissociate a target particle. A trajectory is skipped if the condition (3) does not hold. Following this procedure, it is possible to increase the size of a single batch up to 5×10^7 trajectories and still obtain results within a reasonable time.

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 [20]. 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_4 PES was derived using semi-empirical assumptions, the implementation of empirically derived corrections factors seems to be the most reasonable choice.

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 [15]. 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_2 dissociation. This factor provides an excellent agreement between the QCT method and experimental data for O_2–O dissociation [3]. As will be shown later, the implementation of such a factor in O_2–O_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_2–O_2 collisions can be less efficient than in O_2–O collisions. This statement is based on intuition of strong attraction in the barrierless O_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_4 PES is less reactive than the DMBE O_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_4 PES without additional