



# Investigation of oxygen vibrational relaxation by quasi-classical trajectory method



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## ARTICLE INFO

### Article history:

Received 19 April 2015

In final form 15 July 2015

Available online 29 July 2015

### Keywords:

Quasi-classical trajectory method

Molecular oxygen

Ozone potential surface

Hypersonic flow

Vibrational relaxation

Exchange reaction

## ABSTRACT

O<sub>2</sub>–O collisions are studied by the quasi-classical trajectory method. A full set of cross sections for the vibrational ladder is obtained utilizing an accurate O<sub>3</sub> potential energy surface. Vibrational relaxation is investigated at temperatures between 1000 and 10,000 K, that are relevant to hypersonic flows. The relaxation time is derived based on the removal rate for the first excited vibrational level. A significant deviation from the formula by Millikan and White is observed for temperatures beyond those reported in experimental work. Relaxation becomes less efficient at high temperatures, suggesting that the efficiency of the energy randomization is strongly to the attractive component of the O<sub>3</sub> potential energy surface. These results are explained by analyzing the microscopic parameter of collisions that reflects the number of exchanges in the shortest interatomic distance. The rates of exothermic transitions are found to be nearly independent of the translational temperature in the range of interest.

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## 1. Introduction

During the past several decades, significant progress has been achieved in hypersonic flight technologies. At the same time, it has become clear that further investigation is required in a manner where experiments and theoretical studies are coupled in order to provide reliable and repeatable results. In this sense, the improvement of existing models for simulating the complex aerothermodynamics is of interest for the present hypersonic research. One of the important aspects of hypersonic aerothermodynamics is the energy exchange among the internal degrees of freedom of species behind the shock wave. Since the translational mode can be excited much faster than vibrational, electron–electronic, and, at some conditions, rotational degrees of freedom, it is important to accurately model the energy exchange in order to predict the structure of the shock wave.

Among other phenomena that take place in the shock wave, vibrational excitation and deactivation play an important role in the energy balance. For the past decade, a significant improvement in the fidelity of existing models for air species was accomplished. High fidelity *ab initio* calculations of potential energy surfaces (PES) and application of Monte–Carlo methods became available [13]. A

full set of state-to-state cross-sectional data was obtained for the N<sub>2</sub>–N system under typical shock conditions. An attempt to calculate the dissociation rate of nitrogen under the assumption of a two-temperature model using the quasi-classical trajectory (QCT) method has also been made [2].

Systems that contain oxygen are studied less often, mainly because oxygen quickly dissociates in a strong shock wave. However, during the flight at moderate hypersonic velocities, there is a significant amount of molecular oxygen in the post-shock region. This flight regime is inherent in hypersonic vehicles which travel at a speed of about 2 km/s. Oxygen chemistry is also important in the flight environment of scramjet engines.

The vibrational relaxation time of a significant number of diatomic species, many of which are encountered in hypersonic flows, is adequately described by the formula of [21] (M–W). However, there are several exceptions to this rule. The vibrational relaxation in NO–NO, CO–O, O<sub>2</sub>–O and N<sub>2</sub>–O collisions is several orders of magnitude faster than that of other species. Previously, the M–W equation was extended to all types of collisions in order to model thermal nonequilibrium in strong shock waves [22]. The relation between the macroscopic vibrational relaxation time, gas temperature and pressure, developed by Millikan and White, is based on the analysis of a large amount of experimental data and has the following form:

$$P\tau_{vib} = \exp\left(a\left(T^{-1/3} - b\right) - 18.42\right), \quad (1)$$

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where  $P$  is the pressure in Atmospheres,  $\tau_{vib}$  is the vibrational relaxation time in s,  $a = 0.00116\mu^{1/2}\theta^{4/3}$ ,  $b = 0.015\mu^{1/4}$ ,  $\theta$  is the characteristic vibrational temperature and  $\mu$  is the reduced mass. Eq. (1) suggests that vibrational relaxation becomes more efficient when the gas temperature increases. Existing experimental studies of  $O_2$ -O dynamics in a shock tube [15] were curve fitted by [22] and used to describe experimental data involving air ionization [28]. However, [24] stated that for the interaction of  $O_2$  and O a simple extrapolation of vibrational relaxation time beyond the experimental range of temperature may produce a significant error. Trajectory calculations, performed in [5], support the conclusion that the strong attraction in  $O_2$ -O collisions plays an important role in the vibrational deactivation. Unfortunately, the reported theoretical data covers only a narrow temperature range and addresses deactivation rates only for certain vibrational levels. Thus, the theoretical investigation of thermal nonequilibrium in the  $O_2$ -O system remains an area of interest.

A number of empirical and semi-empirical approaches have been proposed to model vibrational relaxation of air species. It is well known that the applicability of such models is satisfactory only in narrow ranges of temperatures. On the other hand, accurate quantum-mechanical models are available [1] at a very high computational cost. One can consider the quasi-classical trajectory method as a good compromise between accuracy and efficiency. The QCT method generates cross sections for atom-molecule collisions by applying the concept of Monte Carlo simulation and sampling of trajectories over the collision energies for either a specific rovibrational level or at some internal temperature. The QCT method was previously applied to obtain state-to-state rates for collisions between atom and molecule in high temperature air: [3,8,16].

In the work of [8], the QCT simulation of  $O_2$ -O was performed using the three-body potential energy surface by [27]. The rates of transitions between initial rovibrational states and final vibrational states were obtained by summing contributions from any final rotational state, compatible with the final vibrational quantum number. The present work expands the investigation of the  $O_2$ -O system by resolving the rotational structure of transition rates. As will be shown later, the vibration-to-rotation and rotation-to-vibration energy transfers in a system with a zero potential barrier are substantially different from a system with a large repulsive potential. Additionally, special attention in the present paper is drawn to the comparison of obtained vibrational relaxation time with that currently used for hypersonic calculations.

## 2. Background

### 2.1. Experimental studies of $O_2$ -O interaction

The number of experimental studies of oxygen vibrational deactivation by collision with an oxygen atom is very limited. All papers can be divided into two categories depending on the reported temperature range. The first category presents data at atmospheric conditions [14,23]. Relaxation of molecular oxygen is observed through ozone photolysis by laser radiation. The reaction rates are usually limited to temperatures up to 350 K. This experimental data may seem unimportant for hypersonic applications, however, since rovibrational transitions take place even these temperatures, the cross-sectional data for low collision energies (less than 0.1 eV) has a certain influence on the region of moderate temperatures from 1000 K to 5000 K. This fact is important due to the formation of a strong coupling complex by atomic and molecular oxygen at room temperature [24].

The second category of experimental studies reports results on  $O_2$ -O collision dynamics obtained in shock tube facilities. To the

authors' knowledge, only two experimental papers are available at the present time [19,4]. In the work by Kiefer and Lutz, the relaxation of oxygen was measured after the thermal dissociation of ozone in a shock wave. It was found that the relaxation time is several orders of magnitude smaller than in pure oxygen. This conclusion was explained by the presence of a strong chemical effect. The experimental data was then fit to a linear temperature dependence, as given by Eq. (1)

$$\begin{aligned} P\tau_{vib} &= (4.35 \pm 0.19) \times 10^{-8} - (7.75 \pm 0.81) \times 10^{-12}T \text{ atm s,} \\ T &\in 1600 \dots 3300 \text{ K} \end{aligned} \quad (2)$$

However, the technique adopted in [19] contains several important disadvantages. Because the methodology involves ozone, the concentration of atomic oxygen is subject to uncertainty since the rate of the exchange reaction involving  $O_3$  is not well established. Additionally, the thermal dissociation of ozone must occur much faster than  $O_2$  vibrational relaxation, and, thus, the temperature range is very limited. The later experimental measurements of vibrational relaxation time in  $O_2$ -O mixtures were performed in [4]. Atomic oxygen was generated by a RF discharge in a  $O_2$ -Ar mixture. It was found that the relaxation time could be fit by a linear temperature dependence, given by Eq. (1)

$$\begin{aligned} P\tau_{vib} &= (3.06 \pm 0.19) \times 10^{-8} - (2.18 \pm 8.34) \times 10^{-13}T \text{ atm s,} \\ T &\in 1000 \dots 3500 \text{ K} \end{aligned} \quad (3)$$

Comparing Eqs. (2) and (3) one can notice a large difference in the temperature dependence. Breen's data indicates a much weaker dependence of the relaxation time with temperature. The uncertainty range in Eq. (3) allows the possibility for the vibrational relaxation time to increase with the gas temperature.

### 2.2. Theoretical studies of $O_2$ -O interaction

One of the first theoretical investigations of  $O_2$ -O collision dynamics was by [24]. A vibrational deactivation rate was obtained by means of the adiabatic statistical channel model. Comparison of the "Napier" [6] vibrational relaxation time with the existing experimental data [15,4] revealed a difference of the order of two to three times, increasing at high temperature. The theoretical data in [24] is available only at certain temperatures, however, it was shown that the vibrational relaxation rate at room temperature is 3–8 times faster than in the range of temperature from 1500 to 2000 K. While the difference with experiment may be explained by the particular PES used in the calculations, it is certainly clear that the vibrational relaxation is more efficient at low temperatures. This conclusion contradicts the conventional formula, Eq. (1), by Millikan and White.

The study of internal energy transfer in  $O_2$ -O collisions by means of the QCT method was performed in [9,8]. Calculated state-specific cross sections were averaged for each vibrational level, assuming trans-rotational equilibrium. Comparison with other theoretical calculations [17] for the same potential energy surface, revealed a good agreement in multiquantum vibrational deactivation rates as well as thermally averaged dissociation rate. A comparison with the existing experimental data was provided for conditions relevant to ozone formation in the upper atmosphere, and, to a lesser extent, for hypersonic flows.

QCT simulations of the  $O_3$  system were also performed in [12,20]. Ivanov et al. used a newly derived PES for the  $O_3$  system [25]. It was found that the  $O_2$  monoquantum deactivation rate is nearly two times lower than the rate predicted by [24,14]. It is interesting to note that the reported rate is only slightly lower than the rate of  $O_3$  complex formation in the range of temperatures from 100 K to 2000 K. The novel feature introduced in [20] is a straightforward accounting for multiple  $O_3$  PESs. A total of nine

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