



## Rovibrationally detailed cross sections of atom-diatom collisions concerning air species

E. Esposito<sup>(\*)1</sup>, I. Armenise<sup>1</sup>

<sup>1</sup> *Istituto di Metodologie Inorganiche e dei Plasmi del C.N.R., Unita' Territoriale di Bari, via Amendola 122/D, Bari, Italy*

(\*) [fabrizio.esposito@ba.imip.cnr.it](mailto:fabrizio.esposito@ba.imip.cnr.it)

Collisions of atomic oxygen and nitrogen with nitrogen and oxygen molecules respectively have been systematically studied with respect to initial and final vibration of the diatoms by the quasiclassical method, using the best potential energy surfaces available. Cross sections for dissociation, vibrational energy exchange and reaction have been calculated, in a translational energy range up to 10 eV. Comparisons with available thermal data are generally good. Special emphasis has been given to the inclusion of rotation in these calculations, for its importance in dissociation-recombination kinetics.

The collisions of  $O+N_2(v,j)$  and  $N+O_2(v,j)$  ( $v,j$  initial vibrational and rotational quantum numbers) have been studied in a detailed and accurate way, using the quasiclassical method. There are only very sparse results about these systems, despite their importance in atmospheric kinetics. On the contrary, this is the first complete scan of the whole vibrational ladder for these collision processes, including also rotation with a high level of approximation, as will be shown.

For the first collisional system the processes considered are:

$O+N_2(v,j) \rightarrow O+N_2(w)$  non reactive channel  
 $O+N_2(v,j) \rightarrow N+NO(w)$  reactive channel  
 $O+N_2(v,j) \rightarrow O+N+N$  dissociation

For the second system the processes considered are:

$N+O_2(v,j) \rightarrow N+O_2(w)$  non reactive channel  
 $N+O_2(v,j) \rightarrow O+NO(w)$  reactive channel  
 $N+O_2(v,j) \rightarrow N+O+O$  dissociation

( $w$  final vibrational quantum number, atoms and molecules are considered in their respective electronic ground states)

Concerning  $O+N_2$ , The PESs adopted [1] are the best ones currently available for this system. The dynamics is calculated adiabatically on the two PESs ( $^3A''$  ground state,  $^3A'$  first excited state), then the results are summed by weighting the two contribution with appropriate factors [2]. For  $N+O_2$  the PESs used are in [3], with the ground state being  $^2A'$  and first excited state  $^4A'$ . Also in this case two independent sets of results have been obtained on the two PESs, then summed with appropriate factors.

The software used for calculations have been developed entirely in house over the years, tested against many results in literature, and specifically adapted for distributed computations over large grids [4]. Translational energy, considered in the center of mass system, ranges from 1 meV to 10 eV in a continuous way. This range is, at the analysis stage, discretized in 100 bins, but this analysis can be refined if necessary with a finer discretization or with other methods more efficient [5]. Each trajectory is checked at each time step: this procedure, described in [6], then improved in [7], is fundamental for obtaining a good ratio of accuracy over computational time, because the time step is continuously adjusted for the best performance. Uniform density of translational energy of 5000 trajectories per Å of impact parameter, per eV and per each initial state has been used in calculations, that is about 300-400 millions of trajectories and more than one year of cpu for each collisional system.

Both systems have thousands of possible rovibrational states in their respective molecular electronic ground state. Even if all these states were included in calculations as initial ones, it would be extremely difficult to imagine a practical way of exploiting all the details in a kinetic code. The best strategy is to reduce as much as possible the rotational states considered, but retaining anyway many, if not all, details of the rotational distribution. Molecular rotation is particularly important when dissociation-recombination kinetics has to be taken into account [8]. With the approximation used in this work, practically the whole set of rovibrationally detailed cross sections is available starting from “only” 500-600 initial states (that is less than 7% of the total number of possible initial states). The remarkable reliability of the rotational approximation will be shown with some comparisons. The solution to this issue is fundamental for keeping to a manageable amount the computational resources required to complete the whole task, but potentially could be exploited also to manage rotation in kinetic models in a very efficient way.

Excluding very few exceptions, there is no possible direct comparison of state-to-state cross sections for the two systems. On the contrary, *reaction* rate coefficients from specific  $v$  and  $j$  values can be compared with the well known theoretical results of Bose and Candler [9, 10], *if final rovibrational states are summed up* in this work. Very similar trends can be found in this comparison; however, values are different in the two cases, as a consequence of the use of more accurate PESs in this work.

Cross sections for the reactive channel of  $O+N_2$  collisions have been compared with wave packet calculations in [2], with generally good results. Reactivity mechanism is studied in that paper both classically and quantum-mechanically, with very similar results.

Thermal reaction rate for  $O+N_2 \rightarrow NO+N$  is compared with some known values in literature. Thermal rate is obtained here with the appropriate Boltzmann sum over the whole ladder of rovibrational states, in the temperature interval 1000-10000K. In particular, comparison with the review of Baulch [11] is fairly good, while analogous results from Candler and Bose (theoretical data) appear significantly lower.

Dissociation rates from each possible vibrational quantum state for the process  $O+N_2(v, T_{\text{trans}}=T_{\text{rot}}) \rightarrow O+N+N$ , at some ro-translational temperatures have been calculated, and will be shown during the presentation. Unfortunately, the fitting of the first excited PES ( $^3A'$ ) is not as accurate as the one relative to the ground state PES, and this has created some problems with (very) high lying rovibrational states, which are of importance when dealing with state specific dissociation, as will be clear in the presentation. It is important to underline here that rotational temperature can be different from translational one, because data obtained are detailed over the whole set of initial rotational states, while translational temperature can be chosen in a wide range without interpolation, due to cross section calculation in an energy range of 10 eV.

Thermal dissociation rate coefficient for  $O+N_2$  is compared with some known fits in literature based on experimental data (Shatalov [12], Dunn and Kang [13], Park [14]). There is a particularly good agreement with Shatalov results. Detailed dissociation results will be shown during the presentation.

Concerning the non-reactive channel, results agree satisfactorily with experimental data [15] at temperatures higher than 4000K. At room temperature, on the contrary, adiabatic calculations give results lower by many orders of magnitude. This suggests the need for a nonadiabatic approach including the singlet potential energy surface correlating  $N_2O$ , which should introduce a strong vibrational redistribution.

Concerning  $N+O_2$  collisions, a comparison of quasiclassical cross sections with wave packet ones taken from [16] and calculated on the same PESs are shown in fig.1, concerning the reaction process. On the left panel cross sections have been obtained on the ground state PES ( $^2A'$ ), while  $^4A'$  results are on the right panel. The agreement is quite good, in particular for low to intermediate energy values. This is very important for assessing the reliability of quasiclassical calculations, because it is unfeasible to extend in a systematic way quantum calculations to wider energy ranges as well as to higher rotational states.

Thermal reaction rate for  $N+O_2$  collisions is compared with Sayos et al. results by VTST method on the same PESs [3] and experimental data from [11]. The agreement appears quite satisfying, in particular at intermediate temperatures.

State-selected reaction rates can be compared with results from Bose and Candler [10 ONN\_BC]. In this case (differently from O+N<sub>2</sub> case from the same authors) there is a quantitative agreement, in particular for high lying rotational states.

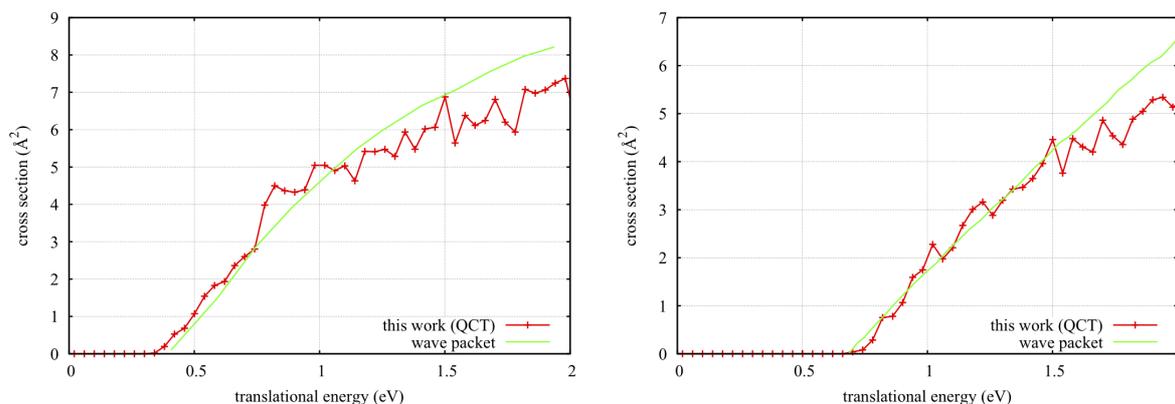


Fig. 1: Cross section comparison between this work (red, with crosses) and wave packet results from Defazio et al., for the process N+O<sub>2</sub>(v=0, j=1)→N+NO. On the left panel: <sup>2</sup>A' PES (ground state), on the right panel: <sup>4</sup>A' PES.

Other relevant results will be shown in the presentation concerning non-reactive process for N+O<sub>2</sub> collisions, for which it is difficult to find similar results in literature.

Comparison of thermal dissociation rate coefficients for N+O<sub>2</sub> is possible with some well known results in literature [12], [13], [14], [17], as a function of temperature in a wide range. Also in this case the agreement is very satisfying.

## References

- [1] P. Gamallo, Miguel Gonzalez, and R. Sayos, *J.Chem.Phys.* 118 (2003) 10602
- [2] S.Akpınar, I.Armenise, P.Defazio, F.Esposito, P.Gamallo, C.Petrongolo, R.Sayós, “Quantum mechanical and quasiclassical Born–Oppenheimer dynamics of the reaction N<sub>2</sub>(X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>)+O(<sup>3</sup>P) N(<sup>4</sup>S) +NO(X<sup>2</sup>Π) on the N<sub>2</sub>O <sup>3</sup>A” and <sup>3</sup>A' surfaces”, *Chem.Phys.*, in press (2012), <http://linkinghub.elsevier.com/retrieve/pii/S0301010411001595>
- [3] R. Sayos, Carolina Oliva, and Miguel Gonzalez, *J. Chem. Phys.*, 117 (2002) 670
- [4] COMPCHEM (<http://compchem.unipg.it/>) and “Bari Computing Center for Science” hosted at INFN-BARI.
- [5] Esposito, F., Atom–Diatom Collision Processes: Rovibrationally Detailed Cross Sections For Models, in: Levin, D.A., Wysong, I.J., Garcia, A.L. (Eds.), *AIP Conference Proceedings*, 1333 (2011) 1357–1364.
- [6] Esposito, F., Capitelli, M., Quasiclassical trajectory calculations of vibrationally specific dissociation cross-sections and rate constants for the reaction O+O<sub>2</sub>(v)→3O. *Chem.Phys.Lett.* 364 (2002) 180–187.
- [7] Esposito, F., Capitelli, M., QCT calculations for the process N<sub>2</sub>(v)+N→N<sub>2</sub>(v')+N in the whole vibrational range. *Chem.Phys.Lett.* 418 (2006) 581–585.
- [8] Esposito, F., Capitelli, M., Selective Vibrational Pumping of Molecular Hydrogen via Gas Phase Atomic Recombination. *The Journal of Physical Chemistry A* 113 (2009) 15307–15314.
- [9] D.Bose, G.V.Candler, *J.Chem.Phys.* 104, 2825 (1996)
- [10] D. Bose and G. V. Candler, *J. Chem. Phys.* 107 (1997) 6136
- [11] D. L. Baulch, C. J. Cobos, R. A. Cox et al., *J. Phys. Chem. Ref. Data* 23 (1994) 847.
- [12] Shatalov, O. P., “Recommended Data on Rate Constants of Physical and Chemical Processes in N–O Atoms System,” *Tech. Rept.*, Moscow State Univ.–Russia, Inst. of Mechanics Avogadro Center (1987)
- [13] M.G.Dunn, S.W.Kang, *Theoretical and Experimental Studies of Re-entry Plasmas*, NASA CR 2232 (1973)
- [14] C.Park, *AIAA* 89-1740 (1989)

- [15] Capitelli, M. Ferreira, C.M., Gordiets, B.F., Osipov, A.I., Plasma Kinetics in Atmospheric Gases, Springer, Berlin (2000), p.110
- [16] P.Defazio, C.Petrongolo, C.Oliva, M.Gonzalez, and R.Sayos, J.Chem.Phys.117 (2002) 3647
- [17] W.C. Gardiner, Combustion Chemistry, Springer-Verlag, Berlin (1984)