

**ISOTOPIC INDISTINGUISHIBILITY, SCATTERING PROCESSES AND THE NON MASS DEPENDENT FRACTIONATION OBSERVED IN OZONE.** P. Reinhardt<sup>1</sup> and F. Robert<sup>2</sup>, <sup>1</sup>Laboratoire de chimie théorique - Université Paris VI (Pierre et Marie Curie) - 4 place Jussieu, case courrier 137 - 75252 Paris ([reinh@mnhn.fr](mailto:reinh@mnhn.fr))  
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**Introduction:** Numerous theoretical models have been proposed to explain the non mass dependent fractionation for oxygen isotopes observed during the synthesis of ozone [1]. The most accepted theory is based on a modification of the standard RRKM model of uni-molecular dissociation [2]. In this theory, when the parameter  $\rho$  (standing for the density of the quantum states of the vibrationally excited ozone) is properly scaled, most observations are reproduced numerically. In the present study, we report an alternative theoretical approach of the non-mass-dependent effect [3] where the calculations are performed using classical trajectories, without adjusting any free parameters.

The scattering is carried out within classical trajectory simulations in an ab-initio potential of the three oxygen atoms in a singlet electronic ground state [4]. All calculations were performed for an initial O<sub>2</sub> with rotational J values up to 25.

**The Principle:** Ozone is produced through the collision O + O<sub>2</sub> with a subsequent stabilization of the activated complex O<sub>3</sub><sup>\*</sup>. Without a stabilizing third body, the complex will break up again into an atom and a molecule. If the isotope distribution of the leaving atom, as function of the energy transfer of the incoming atom to the complex, is different from that of the incoming atom, ozone possibly formed in presence of a stabilizing third body for a given range of energy transfers will be isotopically fractionated. We therefore simulate the scattering and the energy transfer, without an explicit ozone stabilization mechanism. Nevertheless, we take into account the quantum mechanical principle for the indistinguishability of identical isotopes. This effect is enlightened in the present calculation by identifying the 3 isotopes of oxygen by their names and not anymore by their masses. We will show that this principle alone could be at the origin of the non mass dependent isotope effect.

Consider the collision in the laboratory frame where molecules and atoms have an energy  $E_{mol} = 0$  and  $E_{in}$  respectively before the collision (to ease the presentation of the effect  $E_{mol} = 0$  i.e. J=0). After the collision the atom has an energy  $E_{nr}$  if no exchange takes place (nr stands for non-reactive) or an energy  $E_r$  in case of exchange (r for reactive). For a situation with perfectly identifiable atoms – as for example the scattering of <sup>17</sup>O with <sup>16</sup>O<sup>16</sup>O –

the transfer of energy is  $\Delta E_{nr} = E_{in} - E_{nr}$  or  $\Delta E_r = E_r$ . The probability  $f_T(\Delta E)$  (T stands for Total) of having an energy transfer  $\Delta E = \Delta E_r = \Delta E_{nr}$  is then the sum of the two probabilities  $f_{nr}(E_{in} - \Delta E)$  and  $f_r(\Delta E)$ :

$$f_T(\Delta E) = f_{nr}(E_{nr}) + f_r(E_{nr}) \\ = f_{nr}(E_{in} - \Delta E) + f_r(\Delta E)$$

For the scattering of identical isotopes, we do not have the possibility to identify the leaving atom found at E : either it arises from the transfer of  $\Delta E_r$  or  $\Delta E_{nr}$ ; similarly for  $E_{in} - E$ . Therefore we take into account all the 4 possibilities to calculate the probability  $f_i(\Delta E)$  (i stands for indistinguishable isotopes):

$$f_i(\Delta E) = \\ \frac{1}{2} [ f_{nr}(E_{in} - \Delta E) + f_r(\Delta E) + f_{nr}(\Delta E) + f_{nr}(E_{in} - \Delta E) ] \\ = \frac{1}{2} [ f_T(E_{in} - \Delta E) + f_T(\Delta E) ]$$

If the ratio  $f_i(\Delta E) / f_T(\Delta E)$  is  $\neq 1$ , the activated complex is fractionated relative to atoms and molecules. We will show that the calculated variations of this ratio with  $\Delta E$  lie in the domain of the observed compositions for ozone.

In most models, the difference in the life times between symmetrical and non-symmetrical activated complexes is the central parameter that governs the isotope effect. Therefore, following the same principle than that for the energy transfer, we will show the results of life-time calculations for complexes formed by collisions involving dis- and indistinguishable isotopes.

If correct, the present theoretical effect has interesting implications for the chemical reactions at the origin of the <sup>16</sup>O variations observed in solar system materials.

### Experimental

Beside having a theoretical treatment that reproduces numerically the observed ozone compositions, we have attempted to perform an experiment that produces the same effect but via a simpler mechanism than the ozone formation. A 0.1 to 1.0 MeV oxygen beam passes through CO and scattered atoms are implanted into a gold foil with the aim of performing their isotopic analyses by depth profiling with the ion microprobe.

**References:** [1] Thiemens M.H., Heidenreich III J.E. (1983) *Science* 219, 1073-1075. [2] Gao Y.Q., Marcus R.A. (2002) *J. Chem. Phys.* 116, 137-154. [3] Robert F., Camy-Peyret C. (2001) *Ann. Geophys.* 19, 1-16. [4] Schinke R., Fleurat-Lessart P. (2004) *J. Chem. Phys.* 121, 5789-5793.