Mass independent isotope fractionation in ozone; Cosmochemical implications

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A possible origin for the mass independent isotope fractionation term η identified during the synthesis of ozone was proposed based on the conjecture that the probabilities to select the lifetimes τ of the different isotopomers of the complex O₃* - later stabilized as ozone - cannot be the same if O₃* results from reactions involving dis- or indistinguishable isotopes. Accordingly, η was assigned to be equal to the ratio τ/τ_{Indist}. Using a detailed potential for the reaction O+O₂→O₃* the relation between η and τ were calculated for a Boltzmann distribution. It was shown that, in the lifetime domain between 1 and 30 μsec - i.e. where O₃* can be stabilized by a collision with a third body - η was commensurable with experimental data i.e. lies between 1.00 and 1.30.

A nominal value of 1.20 was attributed to η based on the experimentally observed isotope fractionation of ¹⁶O¹⁷O¹⁸O for which the difference in the zero point energy (ΔZPE) is equal to 0 (reported in bold in Table 1). In Table 1, it is assumed that η is constant (η = 1.20) for all the other reactions having (ΔZPE ≠ 0). The numerical results are in agreement within ±5% with the experimental data.

However, some complexes are formed only by reactions between indistinguishable isotopes (noted I in the Table 1). We have thus calculated the ratio τ_{Indist (M1)}/τ_{Indist (M2)} by taking into account the isotopic masses of the reactants. Such a calculation is specific to the formalism developed in the present theory and no adjustment on experimental results was implemented. Numerical results (last four complexes in Table 1; (ΔZPE = 0) are nevertheless close to experimental data and confirm the predictive power of the conjecture.

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<th>Reactions</th>
<th>Complex</th>
<th>ΔZPE</th>
<th>η (MD)</th>
<th>η</th>
<th>α (calc.)</th>
<th>α (mes.)</th>
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Table 1: ΔZPE: the difference in zero-point energies; α(MD): the calculated mass-dependent fractionation factor; η: the mass independent fractionation term; α(calc.): the overall calculated isotopic fractionation factor; α(calc.) = η x α(MD); α(mes.): the measured isotopic fractionation factor; last column: the type of reaction. R and NR for reactive and non-reactive, I for indistinguishable. The reference reaction in bold is shown by a (*). The masses of the reactants are taken into account in the calculation of η for the last four complexes resulting exclusively of reactions between indistinguishable isotopes.