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 O_3* - later stabilized as ozone - cannot be the same if O_3* 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 $O+O_2 \rightarrow O_3$* the relation between η and τ were calculated for a Boltzmann distribution. It was shown that, in the lifetime domain between 1 and 30 *psec* - i.e. where O_3* 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 $^{16}O^{17}O^{18}O$ 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 $\neq$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 $\tau_{Indist\ (M1)} / \tau_{Indist\ (M2)}$ 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.

Reactions		Complex	ΔZPE	α(MD)	η	α (calc.)	α (mes.)	
16	**17-18**	**16-17-18(*)**	**0**	**1.00**	**1.20**	**1.20**	**1.20(*)**	
16	17-17	16-17-17	11.79	1.13	1.20	1.36	1.23	NR+R
16	18-18	16-18-18	22.76	1.26	1.20	1.51	1.50	NR+R
17	16-16	17-16-16	-11,62	0.87	1.20	1.04	1.03	NR+R
17	18-18	17-18-18	10.80	1.12	1.20	1.35	1.31	NR+R
18	16-16	18-16-16	-22,10	0.75	1.20	0.90	0.92	NR+R
18	17-17	18-17-17	-10.64	0.88	1.20	1.05	1.03	NR+R
18	18-16	18-18-16	-22,76	0.74	1.20	0.89	0.92	NR+R
16	16-18	16-16-18	22.10	1.25	1.20	1.50	1.45	NR+R
16	18-16	16-18-16	0	1.00	1.049	1.049	1.08	I
17	17-17	17-17-17	0	1.00	1.021	1.021	1.02	I
18	18-18	18-18-18	0	1.00	1.025	1.025	1.03	I
18	16-18	18-16-18	0	1.00	1.027	1.027	1.04	I

Table 1: ΔZPE: the difference in zero-point energies; a(MD): the calculated mass-dependent fractionation factor; *h*: 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.