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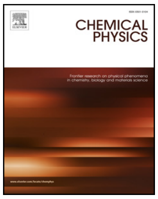

On the mass independent isotope fractionation in ozone

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ABSTRACT

The theoretical approach developed by the authors in order to account for the mass independent isotopic fractionation observed in ozone is applied taking into account explicitly the isotopic masses of the reactants and the relative positions of the oxygen atoms in O_3. From classical trajectory calculations on the potential surface of Schinke et al. for the collision $O + O_2 \longrightarrow O_3^* \longrightarrow O + O_2$, a supposed quantum effect is simulated, resulting in different average lifetimes for the intermediate complex when its formation involves collisions between distinguishable or between indistinguishable isotopes. The stabilization of the complex by a third body $M(O_3^* + M \longrightarrow O_3 + M)$ is assumed to involve only the inelastic collisions. Under this assumption, we show that the effect of indistinguishability, the ΔZPE correction, and by taking into account the explicit masses of the reactants, reproduce (in the order of importance) the experimental results within ± 2%. An alternative definition of the lifetime of the complex reduces the number of apparently free parameters in the calculations.

1. Introduction

In clear contradiction with the usual mass dependent isotopic fractionation theory [1–3] a mass independent effect for oxygen isotopes was reported for ozone [4]. This discovery has then stimulated numerous experimental verifications [5–18]. Although extensive theoretical efforts have been spent on this effect [19–33] the origin of the mass independent term remains not understood. In this paper, we test a previously proposed mechanism [34] by numerical comparisons with measured isotope effects in several well documented experimental situations, taking now into account explicitly the isotopic masses of the reactants. The stabilization of the activated complex O_3^* to form ozone O_3 depends on its lifetime that allows collision with a third body M to avoid spontaneous re-dissociation into $O + O_2$:

$$O + O_2 \longrightarrow O_3^* \xrightarrow{+M} O_3 \qquad (1)$$

It was suggested already long ago [35] that quantum symmetry selection rules may play a central role during the process of stabilization of the complex O_3^* by collisions with the bath gas M. Indeed, in symmetric molecules some excited state are inaccessible [36] which could lead to lower recombination rates [37] for the symmetrical isotopomers of ozone relative to non-symmetrical ones. However, despite of important computational efforts, no isotope effect due to symmetry was found [22]. Among the numerous proposals published in the literature to account for the mass independent fractionation term (referred to as η) two sets of interpretations are now available:

1. On one hand extensive calculations have come to the conclusion that the mass independent effect cannot be explained by statistical reaction rate theories [25,20,28,33,38]. Accordingly, on the basis of numerical results, it was shown [21] that the lifetimes of the scattering resonances depend on their rotational excitation implying in turn, that molecular symmetry could be at the origin the factor η in the overall isotopic fractionation factor. However, most of these theoretical studies have only considered the possible isotope exchange reactions between O, O_2 or O_3 and have recognized that when η is considered as a free parameter and adjusted empirically to 1.15 most of the experimental data are reproduced numerically [24].
2. On the opposite, we have suggested [34] that the isotope effect can be approximated by classical mechanical calculations with an additional ad hoc modification for the quantum–mechanical indistinguishability in scattering processes. Under these conditions η is not anymore considered as a free parameter but calculated in the framework of classical mechanics. Interestingly, Rao et al. [39] have verified through a quantum mechanical calculation that this proposal yields numerically important differences in the reaction rates of O_3^* formed by collisions involving dis- or indistinguishable isotopes. Note that this effect is distinct from the quantum selection rules involved in molecular symmetry

In the present paper, we extend our previous calculations, now taking into account the isotopic masses of the reactants involved in the

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formation of the complex, and combine these with the mass-dependent isotopic fractionation factors previously reported in the literature [28]. We show that both, indistinguishability in scattering processes and masses, together with the correction due to differences in zero-point energies (ΔZPE), reproduce quite correctly most experimental data.

2. Theory

The formalism developed elsewhere [34] is briefly recalled here. Consider the two different reactions between the fully distinguishable oxygen isotopes ^{16}O, ^{17}O, ^{18}O, involved in the formation of an activated complex $[OOO]^*$.

$$^{16}O + {}^{17}O^{18}O \rightarrow [^{16}O^{17}O^{18}O]^* \rightarrow {}^{16}O + {}^{17}O^{18}O \tag{2}$$

$$^{16}O + {}^{17}O^{18}O \rightarrow [^{16}O^{17}O^{18}O]^* \rightarrow {}^{18}O + {}^{17}O^{16}O \tag{3}$$

At this stage, the relative positions of the different isotopes in the complex $[OOO]^*$ are not taken into account, nor the third channel giving a single ^{17}O. The atom-molecule interaction (2) does not yield an isotope exchange, while in the reaction (3), an isotope is exchanged between O and O_2. The processes (2) and (3) are noted NR (non-reactive) and R (reactive), respectively. Although the non-reactive process (2) is not involved in an isotope exchange, the corresponding complex O_3^* may participate to the formation of O_3 via its stabilization; hence the NR O_3^* must be taken into account in the final isotopic composition of O_3. The activated complex O_3^* has an average lifetime $\bar{\tau}$ dictated by the relative contributions of the lifetime of the non-exchange or non-reactive (noted $\bar{\tau}_{NR}$) and of the exchange or reactive processes (noted $\bar{\tau}_R$). Let us designate with $f(\tau)$ the distribution of lifetimes τ of complexes in a thermal gas following Boltzmann's statistics, separately for NR and R processes and noted as $f_{NR}(\tau)$ and $f_R(\tau)$, respectively. We assume that O_3^* can be stabilized only beyond a minimum lifetime τ_{Min}, leading to O_3. In other terms, any O_3^* with a lifetime $\tau < \tau_{\mathrm{Min}}$ re-dissociates spontaneously before encountering a third body.

Let us note $\bar{\tau}_{NR}$ the average lifetime for the NR complex and P_{NR} the relative proportion of non-reactive collisions that contribute to $\bar{\tau}_{NR}$ among all the possible non-exchange collisions of the Boltzmann distribution. These definitions correspond to:

$$\bar{\tau}_{NR}(\tau_{\mathrm{Min}}) = \int_{\tau_{\mathrm{Min}}}^{\infty} \tau f_{NR}(\tau)\,d\tau \Big/ \int_{\tau_{\mathrm{Min}}}^{\infty} f_{NR}(\tau)\,d\tau \tag{4}$$

$$P_{NR}(\tau_{\mathrm{Min}}) = \int_{\tau_{\mathrm{Min}}}^{\infty} f_{NR}(\tau)\,d\tau \Big/ \int_{0}^{\infty} f_{NR}(\tau)\,d\tau \tag{5}$$

We define as well

$$X_{NR} = \int_{0}^{\infty} f_{NR}(\tau)\,d\tau \Big/ \int_{0}^{\infty} (f_{NR}(\tau) + f_R(\tau))\,d\tau \tag{6}$$

which is independent of τ_{Min}.

These definitions are extended for R in place of NR. The average lifetime $\bar{\tau}(\tau_{\mathrm{Min}})$ of the complex is then the sum of the relative contributions of the reactive and of the non-reactive collisions:

$$\bar{\tau}(\tau_{\mathrm{Min}}) = x\cdot\bar{\tau}_{NR}(\tau_{\mathrm{Min}}) + (1-x)\cdot\bar{\tau}_R(\tau_{\mathrm{Min}}) \tag{7}$$

with

$$x = \frac{X_{NR}P_{NR}}{X_{NR}P_{NR} + X_R P_R} \tag{8}$$

The formula (7) remains exact for calculating average lifetimes in any ensemble of trajectories with lifetimes larger than the limit τ_{Min}. Let us now consider a collision between fully indistinguishable isotopes such as:

$$^{16}O + {}^{16}O^{16}O \rightarrow [^{16}O^{16}O^{16}O]^* \rightarrow {}^{16}O + {}^{16}O^{16}O \tag{9}$$

As illustrated schematically in Fig. 1, it is impossible in quantum mechanics to ascribe the emerging ^{16}O to a R or a NR collision. We average thus over P_{NR} and P_R like

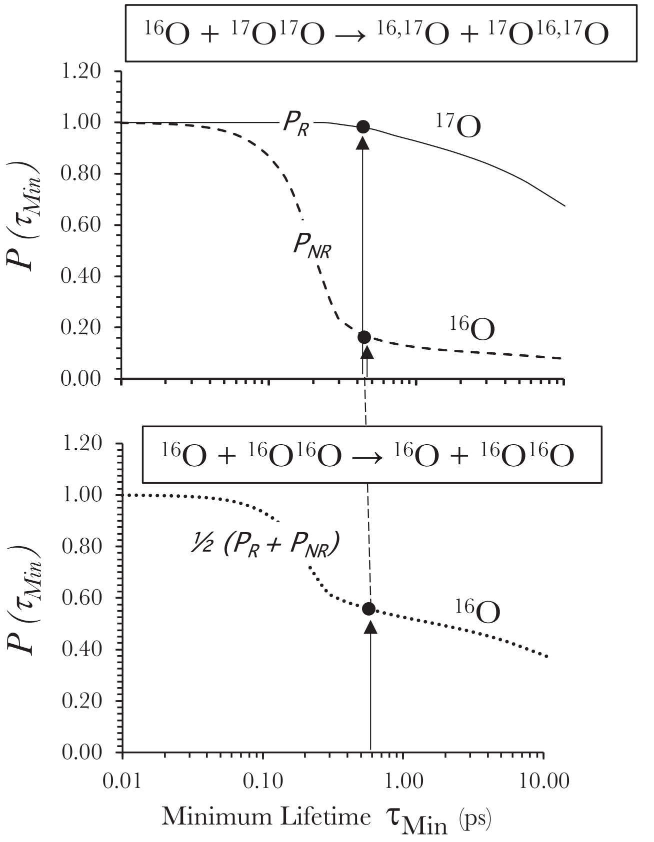

Fig. 1. A schematic drawing to illustrate the isotope effect used in this paper to calculate the lifetimes of the complex produced by reactions between distinguishable (such as $^{16}O + {}^{17}O^{17}O$, upper part) or indistinguishable isotopes (such as $^{16}O + {}^{16}O^{16}O$, lower part). Data were computed using the actual potential $O+O_2$, showing the functions P defined in the text, averaged over the Boltzmann distribution; R and NR stand for exchange (Reactive) and non-exchange events (Non-Reactive), respectively. The atoms ^{17}O and ^{16}O emitted by the dissociation of the complex are shown on each curve. For reactions involving indistinguishable isotopes, P_R and P_{NR} contribute both to the lifetime since ^{16}O may be the incident atom or one of the two atoms of the molecule.

$$P_I(\tau_{Min}) = \frac{1}{2}(P_{NR}(\tau_{Min}) + P_R(\tau_{Min})) \tag{10}$$

with the subscript I standing for indistinguishable (see Fig. 1, lower panel). We then replace $P_{NR}(\tau_{Min})$ and $P_R(\tau_{Min})$ by $P_I(\tau_{Min})$ to calculate the lifetime $\bar{\tau}_I(\tau_{Min})$ for O_3^* formed by indistinguishable isotopes. This gives

$$\bar{\tau}_I(\tau_{Min}) = X_{NR}\bar{\tau}_{NR}(\tau_{Min}) + X_R\bar{\tau}_R(\tau_{Min}) \tag{11}$$

Because all the other reaction rate ratios involved in the formation of ozone yield mass dependent isotopic fractionations, the lifetime ratio η of O_3^* formed by dis- and indistinguishable reactions gives directly the mass independent isotope fractionation factor (in the steady-state and low pressure approximation from the ratio of reaction rates [34])

$$\eta(\tau_{Min}) = \frac{\bar{\tau}(\tau_{Min})}{\bar{\tau}_I(\tau_{Min})} \tag{12}$$

The relation between the lifetime of the overall reaction rates for ozone at low pressure can be found in Ref. [34], Eq. (13). It is worth noting that, with the present formalism, the mass balance is exact for $\tau_{\mathrm{Min}} = 0$ leading to $P_R = P_{NR} = P_I = 1$ and $\eta = 1$.

When used with simulations including only one single mass, η can have thus only one single value, η for the 678 case, and furtheron $(1 + 2\eta)/3$ for 667, 668, 677, 688, 778, 788 and 1 for 666, 777 and 888 combinations, leading to a completely mass-independent fractionation, $\eta_{\text{mass-indep.}}$. For $\tau_{\min} = 0$ the mass-independent fractionation factor

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