Abstract  The rate of ozone recombination, \( \text{O}_2 + \text{O} + \text{M} \rightarrow \text{O}_3 + \text{M} \), is strongly sensitive to the masses of the participating oxygen isotopes—the effect ultimately leading to the unconventional fractionations of ozone isotopomers in the Earth atmosphere. The mass dependence for asymmetric molecules is reconstructed, within the strong collision approximation, from the partial widths of narrow resonances of \( \text{O}_3 \) and demonstrated to stem from the contributions of highly rotationally excited ozones.

1 Introduction

Ozone in the stratosphere is formed primarily in the Chapman cycle, i.e. via collisional recombination of the atomic and molecular oxygen:

\[
\text{O}(\alpha) + \text{O}_2(\alpha) \rightarrow \text{O}_3^* (1)
\]

\[
\text{O}_3^* + \text{M} \rightarrow \text{O}_3 + \text{M}. (2)
\]

In (1), ozone above dissociation threshold, \( \text{O}_3^* \), forms from a given arrangement (or isotope-specific) channel \( \alpha \). It can dissociate again unless stabilized in (2) by a collision with the buffer gas M. The incoming oxygen atom in (1) always becomes one of the end atoms of \( \text{O}_3 \) (never the central atom). Likewise, the dissociating \( \text{O}_3^* \) has only two accessible arrangement channels in which one of the end atoms is removed.

An intriguing isotopic fractionation effect in \( \text{O}_3 \) [1] was traced down to the strong sensitivity of the recombination rates in (1–2) to the masses of oxygen isotopes (\( ^{16}\text{O}, ^{17}\text{O}, \text{or} ^{18}\text{O} \), abbreviated as 6, 7, or 8, respectively). Figure 1a shows the room-temperature recombination rates, \( k_{\text{rec}}(k_B T, \alpha) \), measured in various isotope-specific channels \( \alpha \). For the 668 molecule, for example, two such channels are:

\[
8 + 66(ZPE_\alpha) = 866^{(\alpha)} = 86(ZPE_\beta) + 6
\]

The rates in these channels (relative to the ‘standard’ rate of 6+66 \( \rightarrow 666 \)) are substantially different: 0.92 in the left channel versus 1.45 in the right one (Fig. 1a). The measured rates correlate with the asymmetry between the thresholds of the two channels, i.e. with the difference of the vibrational zero-point energies (ZPEs) of the outgoing and incoming diatoms. In the 668 case, the ZPE\(_\alpha\) of the lighter 66 diatom exceeds the ZPE\(_\beta\) of the heavier 68 diatom. The recombination from the ‘heavier’ channel in Eq. (3), where \( \Delta\text{ZPE} = \text{ZPE}_\alpha - \text{ZPE}_\beta > 0 \), is faster than the ‘standard’ (for which \( \Delta\text{ZPE} = 0 \)). Conversely, channels with lighter diatoms (\( \Delta\text{ZPE} < 0 \)) generally
Relative recombination rates versus ZPE difference between the outgoing and the incoming diatomic oxygen molecules, $\Delta ZPE$. Solid symbols are experimental rates [2] for the following reactions (with respective $\Delta ZPE$ in cm$^{-1}$): $8^6 + 66$ and $68 + 8$ ($-23$); $7 + 66$ ($-12$); $88 + 7$ ($+12$); $86 + 6$ and $6 + 88$ ($+23$); open symbols calculations with Eq. (4).

Arrows relate $\Delta ZPE$ values to the calculated isotope-specific channels; b, c branching ratio in the $6 + 68$ channel for resonance states in the $668$ ozone plotted against energy in excess of the lowest ($6 + 68$) dissociation threshold, $E^+$. In b averaging over all $J \leq 40$. In c averaging for fixed $J = 0$ (1), $J = 20$ (2), $J = 40$ (3). Arrow marks the position of threshold for $8 + 66$.

lead to slower recombinations. This almost linear dependence of $k_{rec}(\alpha)$ on $\Delta ZPE$ is surprisingly steep and significantly exceeds the expected ratio of $\exp(\Delta ZPE/k_B T) \sim 1.1$ (the threshold asymmetry, $\Delta ZPE \approx 23$ cm$^{-1}$, is much smaller than both $k_B T \approx 200$ cm$^{-1}$ or the depth of the ozone well, $V_0 \approx 9,000$ cm$^{-1}$). The $\Delta ZPE$-dependence has been extensively investigated using statistical models [3] and classical mechanics [4]. Quantum scattering calculations performed for a non-rotating ozone (see, e.g. [5]) did not provide a consistent explanation of the observed rates [4]. The aim of this communication is to demonstrate that the treatment of the association step (1) in terms of resonances in rotationally excited O$_3$ is capable of reproducing the experiment.

2 Resonance Recombination in the Strong Collision Approximation

The full quantum treatment of the reactions (1–2) is still beyond the power of present-day computers. The problem is made tractable by first introducing the strong collision approximation (SCA) [6] and replacing the step (2) with a model stabilization probability. Next, the step (1) is assumed to be dominated by isolated narrow resonances, the only stabilizable states above threshold. The absolute thermal rate constant $k_{rec}(k_B T, \alpha)$ becomes a sum over individual contributions of resonance states, $[E_n(J), \Gamma_n(J)]$, calculated for a fixed total angular momentum $J$ of O$_3$ [6]:

$$ Q_r(\alpha)k_{rec}(k_B T, \alpha) = \sum_J (2J + 1) \sum_n \frac{\Gamma_n(\alpha; J)}{\omega + \Gamma_n(J)} \frac{\omega}{\omega} \exp(-E_n(J)/k_B T) $$

Here $Q_r(\alpha)$ is the O/O$_2$ partition function, $\Gamma_n(\alpha; J)$ is the partial resonance width in channel $\alpha$, and $\omega$ is the frequency of ‘strong collisions’ with M. The problem (1–2) reduces to calculation of near-threshold resonance states in the isolated rotating O$_3$. In the experimentally relevant low-pressure limit, $k_{rec} \sim \omega$, and the relative rates are independent of the SCA parameter $\omega$.

Dynamics calculations are performed using a modified version of the accurate three-dimensional ozone potential [4] supporting $\sim 250$ bound states. Shallow van der Waals wells in the asymptotic channels are eliminated and only one permutation is considered. The molecular Hamiltonian in Jacobi coordinates is set in the discrete variable representation and made complex symmetric using an optical potential in each channel $\alpha$.

There is a second isotope effect in Fig. 1a. All molecules with identical end atoms (‘symmetric’ $666$, $686$, $868$, etc.)—for which $\Delta ZPE = 0$—fall out of the linear $\Delta ZPE$-dependence. Their recombination is apparently less efficient (by about 15%) than for asymmetric isotopomers. This ‘symmetry’ or ‘mass-independent’ effect is not considered in this work.
The time-dependent Schrödinger equation is solved and the complex eigenvalues are retrieved with filter diagonalization [7]. Only narrow states with $\Gamma_n \lesssim 1 \text{ cm}^{-1} \ll \Delta \text{ZPE}$ are considered. Two additional calculations for each $J$ are performed to estimate the partial widths $\Gamma_n(\alpha)$ and $\Gamma_n(\beta) = \Gamma_n - \Gamma_n(\alpha)$ from perturbation theory. The coupling to products in the optical Hamiltonian is slightly rescaled either in one ($\alpha$) or in the other ($\beta$) arrangement channel, and $\Gamma_n(\alpha)$ is evaluated from the variations, $\delta(\alpha, \beta) \Gamma_n$, of the imaginary parts of the eigenvalues:

$$\frac{\Gamma_n(\alpha)}{\Gamma_n} = \frac{\delta(\alpha)}{\delta(\alpha) + \delta(\beta)} \frac{\Gamma_n}{\Gamma_n(\alpha)}.$$

### 3 Results and Discussion

Resonance spectra for $J \leq 40$ are calculated for three isotopomers: 666, 668 and 667. About 6,000 resonances are calculated for each molecule. The model is trustworthy and the relative rates based on Eq. (4) (Fig. 1a) agree with experiment to within 80%. The $\Delta \text{ZPE}$-dependence is reproduced remarkably well: the recombination from the ‘lighter’ channels ($\Delta \text{ZPE} > 0$) is significantly faster than from the ‘heavier’ channels ($\Delta \text{ZPE} < 0$).

The explanation of the strong impact which tiny $\Delta \text{ZPE}$ asymmetries have on $k_{\text{rec}}(k_B T; \alpha)$ is provided by Fig. 1b, c showing—for 668—the branching ratio in the lowest channel, $G(6 + 68) = \langle \Gamma(6 + 68)/\Gamma \rangle$, versus energy in excess of the $6 + 68$ threshold; $G(6 + 68)$ in Fig. 1b is averaged over narrow energy windows containing many resonances with all $J \leq 40$. The lowest channel is preferentially populated near threshold, $G(6 + 68) \sim 1$. As energy increases, $G(6 + 68)$ slowly decreases and reaches the value of 0.5—both arrangement channels become statistically equivalent. The statistical limit is reached, however, only $500 \text{ cm}^{-1}$ above threshold, high above $\Delta \text{ZPE}$: the asymmetry ‘spreads’ across a broad energy range. The effect is markedly $J$-dependent, as illustrated by $G(6 + 68)$ plotted for selected $J$ values in Fig. 1c. The higher $J$, the higher the energy, at which the two channels equilibrate. The reason are the centrifugal barriers building up in both arrangement channels and reaching deep into continuum. Their heights, which mark the effective thresholds, remain separated by $\sim \Delta \text{ZPE}$.

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