The origin of anomalously large enrichments of stratospheric ozone in heavy isotopes has been a mystery for more than 25 years. The isotope $^{16}$O is dominant in the atmosphere, so that most oxygen molecules ($O_2$) consist of two $^{16}$O atoms. However, stratospheric ozone ($O_3$) is surprisingly observed to be heavily enriched in the isotopes $^{17}$O and $^{18}$O relative to the atmospheric oxygen from which it’s formed. Careful experimental studies have shown that the recombination reaction that forms ozone, $O_2 + O + M \rightarrow O_3 + M$, is responsible for the effect. The recombination rates for various isotopic combinations differ by more then 50%, which is a remarkably large isotope effect taking into account small mass difference. A clear explanation for the effect is given in terms of the energy transfer mechanism, where the metastable $O_3^*$ states of ozone are formed first and then stabilized by collisions with M. Sophisticated treatment is employed, which considers different metastable states as different species, with their energies and lifetimes obtained from accurate quantum scattering calculations.

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