Quantum origin of anomalous isotope effect in ozone formation

Dmitri Babikov

Abstract:

The origin of anomalously large enrichments of stratospheric ozone in heavy isotopes has been a mystery for 20 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. Populations of the metastable states is found to build up and then decay back to O_2 + O through several possible channels. When different isotopes of oxygen are involved the channels become open at different energies due to the differences in quantum zero-point energies (ΔZPE) of different O_2 molecules. The spectrum of metastable states is anomalously dense below the ΔZPE threshold, and these states are accessible only from the lower entrance channel. Also, the metastable states in the ΔZPE part of spectrum are stabilized very efficiently by collisions because they are energetically close to the bound O_3 states. Such processes significantly enhance the formation rates of ozone isotopologues through the lower energy channels. This finding finally explains the anomalous isotope effects observed in many experiments.