

ABSTRACT
TOWARD UNDERSTANDING THE ORIGIN OF MASS-INDEPENDENT
FRACTIONATION IN SULFUR ALLOTROPES AND IN OZONE

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Mysterious isotope effects, found in atmospheric ozone, cannot be explained by the standard mass-dependent statistical model. Similar mass-dependent isotope effects were also uncovered in sulfur deposits older than 2 billion years. In an effort to pinpoint possible reasons of these isotope effects, we build a theoretical description of the recombination reactions in sulfur allotropes and in ozone. No potential energy surface exists for the sulfur allotropes, so electronic structure calculations are also required. Ab initio calculation of two dimensionally reduced (2D and 3D) models of the potential energy surface for the tetrasulfur molecule at CCSD(T)-F12 and MRCI levels of theory are considered here. The 2D model is used to calculate the vibrational states energies up to 2000 cm^{-1} . Normal mode analysis indicates that the two considered modes in S_4 represent a significant mixture of conventional bending and stretching motions. Analysis of the bound vibrational state properties in ozone reveals that the ratio between the number of states in asymmetric and symmetric ozone molecules deviates noticeably from the statistical factor of 2, but in different directions for the singly- and doubly-substituted molecules. However, in the upper part of the spectrum both singly- and doubly-substituted species behave in the same way, which can be a factor contributing to the isotope effects in ozone. Rotation-vibration coupling and its implications for the isotope effects have been studied in detail for ozone isotopomers for both bound states and scattering resonances, using uncoupled, partially coupled and fully coupled approaches. We found that the effects of rovibrational coupling are minor for low values of J , but become more significant for large values of J . However, these effects are rather uniform for both symmetric and asymmetric ozone isotopomers, therefore we conclude that the Coriolis coupling does not seem to favor the formation of asymmetric ozone molecules and cannot be responsible for symmetry-driven mass-independent fractionation of oxygen isotopes. A general program for calculation of energies and lifetimes of bound rotational-vibrational states and scattering resonances for ABA/AAB-type systems is developed (SpectrumSDT). The data calculated by this program can be useful for spectroscopic analysis and prediction of reaction rates.