

Abstract

The thesis is focused on the theoretical study of the isotope effects in three atmospheric reactions, the CO+OH reaction, the photolysis of N₂O, and the ozone formation. The CO+OH reaction is investigated by using both Rice-Ramsperger-Kassel-Marcus theory and its nonstatistical modification, which was prompted by existing molecular-beam data on incomplete intramolecular energy transfer in the HOCO* intermediate. The resulting calculations show reasonable agreement with most experimental data, except the O isotope effect. Two predictions are made: the temperature dependence of the OD+CO reaction; and the rate constant k_v decreasing with increasing CO vibrational quantum number v from $v = 0$ to $v = 1$. In both experiments and our calculation, the kinetic oxygen isotope effect is different from the expected value (i.e. the mass-dependent slope), which may be due to the H-tunneling. An experiment that avoids a possible role of vibrationally excited OH radicals as reactants in the O isotope effect is also suggested to remove the discrepancy in the O isotope effect between the experiments and calculations.

The UV photolysis of the greenhouse gas N₂O and its isotope effects are important in atmospheric chemistry. Based on the multidimensional reflection principle using the available *ab initio* data on the molecule for the potential energy surfaces and the transition dipole moments, we provide an accurate but not computationally intensive method in obtaining the absorption cross section. The present calculated fractionation gives good agreement with the experimental absorption cross section in the low-energy region, where the experimentally observed isotopic fractionation occurs. We also suggest a single effective mass, a linear combination of two main coordinates for the photolysis, to determine the slope of a multi-element isotope plot and to yield approximate agreement between the experimental data and a “mass-dependent” fractionation, which range from 0.47 to 3.28.

A modified *ab initio* potential energy surface is used for calculations of ozone recombination and isotopic exchange rate constants. The calculated low-pressure isotopic effects on the ozone formation reaction are consistent with the experimental results and with the theoretical results obtained earlier [J. Chem. Phys. **116**, 137 (2002)]. This result showed that they are relatively insensitive to the properties of the PES.

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