

A new source of OH radicals in the stratosphere and mesosphere

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OH radical in the terrestrial atmosphere plays a critical role in initiating the oxidation of a variety of trace gases such as organic compounds and anthropogenic gases and thus in removing them from the atmosphere. The atmospheric OH radical production occurs from the formation of the electronically excited oxygen O(1D) atoms in the ultraviolet photolysis of ozone, followed by the chemical reaction of the O(1D) with H₂O, H₂, and CH₄, while most of the O(1D) atoms produced photolytically are quenched to O(3P) atoms by collisions with air molecules of N₂ and O₂.

Above 60 km the photochemical destruction of H₂O also produces OH radicals. There is a serious dilemma for understanding of the OH chemistry in the middle atmosphere. The satellite observations have indicated the OH densities around 40 km in the stratosphere are several ten percent higher than predicted by standard photochemical theory, while those in the mesosphere (50-80 km) are lower than the theoretical prediction. It is thus quite important to study the photodissociation processes of ozone in the ultraviolet region. We have examined the photodissociation processes of ozone in the ultraviolet region by laboratory studies using a vacuum ultraviolet laser-induced fluorescence technique for the direct detections of nascent O(1D), O(3P) and O(1S) atoms. The wavelength tunable coherent VUV radiation was obtained by two-photon resonance four-wave frequency mixing technique in Kr. We have determined the quantum yield of the O(1S) atoms in the photolysis of ozone to be $(2.5 \pm 1.1) \times 10^{-3}$ at 193 nm.

The O(1S) quantum yield in the photolysis of ozone is quite small. Nevertheless, we have found the reaction process of O(1S) with H₂O can be a very efficient OH formation source around 40 km using simple model calculations. This is because the de-excitation of O(1S) by air molecules of N₂ and O₂ is very slow, while the reaction rate of O(1S) with H₂O is relatively fast. We have estimated the formation of OH radicals by the reactions of O(1S) + H₂O is at most about 14 % of those of O(1D) + H₂O around 40 km, while the contribution of O(1S) + H₂O is smaller at around 70 km. This finding can be a solution of the HO_x dilemma.