UV-photoexcitation of oxygen-isoprene collision complexes as a source of singlet oxygen

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The interaction of oxygen molecules with molecular environment provides the strong enhancement of UV-absorption by oxygen and other molecules which takes place when molecules collide in the gas phase. Thus, isoprene C_5H_8 (the most widespread biogenic organic compound in the Earth atmosphere after methane), being transparent at wavelengths λ>240 nm, absorbs in the presence of molecular oxygen due to collision-induced absorption in C_5H_8-O_2 collision complexes [1].

Oxygen collision-induced absorption also dramatically changes oxygen photochemistry causing new photochemical processes such as formation of singlet oxygen species $^1O_2$ which possess high chemical reactivity and play important role in nature. Recently we have observed $^1O_2$ formation as result of the isoprene-oxygen collision complexes photoexcitation in the gas phase within the spectral region 253.5−355 nm at the oxygen elevated pressure [2]. Singlet oxygen has been detected with its NIR luminescence centered near 1.27 μm. The $^1O_2$ photogeneration is found to be a one-photon process. We have measured the $^1O_2$ quantum yield within the UV-C region (253−278 nm) and supposed it is governed mainly by O_2 molecules photoexcitation to the Herzberg III ($^3\Delta_u$) state via C_5H_8-O_2 collision complexes enhanced absorption. So excited triplet O_2 gives rise to $^1O_2$ because of triplet-triplet annihilation in the collisions with unexcited O_2 molecules. In the UV-B (308 nm) region the $^1O_2$ appearance is attributed to the excitation of a double spin−flip (DSF) transition in C_5H_8-O_2 complex. In the UV-A region (355 nm) besides DSF isoprene sensitizes $^1O_2$ formation as result of O_2-assisted excitation to the triplet state. We suppose that DSF may result in $^1O_2$ formation in widespread wavelength region depending on oxygen collisional partner X in any oxygen-containing media. Relying on the obtained data we made estimations of the role of this new process in the Earth atmosphere.

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