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Nighttime atmospheric chemistry of iodine

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Little attention has so far been paid to the nighttime atmospheric chemistry of iodine species. Atmospheric models predict a buildup of HOI and I2 during the night that leads to a spike of IO at sunrise, which is not observed by measurements. In this work, electronic structure calculations are used to survey possible reactions that HOI and I2 could undergo at night in the lower troposphere, and hence reduce their nighttime accumulation. The new reaction $NO_3 + HOI \rightarrow IO + HNO_3$ is proposed and included in two atmospheric models, along with the known reaction between I2 and NO_3 , to explore a new nocturnal iodine radical activation mechanism. Our results show that this iodine scheme leads to a considerable reduction of nighttime HOI and I2, which results in the enhancement of more than 25% of nighttime ocean emissions of HOI + I2 and the removal of the anomalous spike of IO at sunrise. That active nighttime iodine could also have a considerable, so far unrecognized, impact on the reduction of the NO₃ radical levels in the marine boundary layer (MBL) and hence upon the nocturnal oxidizing capacity of the marine atmosphere. The effect of this is exemplified by the indirect effect on dimethyl sulfide (DMS) oxidation.