Ozone photo-dissociation - revisited

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We present new, high-resolution determinations of the quantum yield of O(1D) production, Φ(O1D), in the photo-dissociation of ozone between 300 nm and 400 nm. Φ(O1D) is also determined as a function of temperature (200 K to 600 K) between 308 nm and 325 nm over the region associated with the vibrationally-enhanced photodissociation channel leading to O(1D) + O2(a1Δg). Quantum yield determinations at room temperature are extended beyond 325 nm to visible wavelengths over which only the spin-forbidden channel leading to O(1D) + O2(X3Σg−) is operative.

The relative yields of O(1D) and total O (represented by O(3P) once O(1D) is quenched) are determined by chemiluminescence of respectively CF2(1B1) CF2(3B1) resulting from the reactions of O(1D) and O(3P) with C2F4. This method proves to be very sensitive towards O(1D) and O(3P). Combination of both detection methods provides a highly sensitive technique for determining the Φ(O1D) of O3 photolysis; the major advantages are that our technique does not require any external excitation for O-atom detection nor the knowledge of the ozone absorption cross-section, laser energy, or amounts of ozone photolysed.

Accurate Φ(O1D)(T) determinations were enabled using a specially-designed temperature-graded reaction cell with parallel simultaneous detection of O(1D) at different sections (temperatures) of the reaction chamber using a series of photomultiplier tubes. The results are compared to the recent ab initio quantum mechanical study of the O(1D) formation in the photolysis of ozone by Grebenshchikov and Rosenwaks [1].

References