Ozone photo-dissociation - revisited

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We present new, high-resolution determinations of the quantum yield of $O(^1D)$ production, $\Phi(O^1D)_\lambda$, in the photo-dissociation of ozone between 300 nm and 400 nm. $\Phi(O^1D)_\lambda$, 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 $O(^1D) + O_2(a^1\Delta_g)$. Quantum yield determinations at room temperature are extended beyond 325 nm to visible wavelengths over which only the spin-forbidden channel leading to $O(^1D) + O_2(X^3\Sigma_g^-)$ 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 $CF_2(\tilde{A}^1B_1)$ $CF_2(\tilde{\alpha}^3B_1)$ resulting from the reactions of $O(^1D)$ and $O(^3P)$ with C_2F_4. 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 $\Phi(O^1D)_\lambda$ of O_3 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 $\Phi(O^1D)_\lambda(T)$ 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

(1) Grebenshchikov, S. Y.; Rosenwaks, S. *J. Chem. Phys.* **2010** 114 , 9809-9819.