PRECISE MEASUREMENTS OF ABSORPTION CROSS-SECTIONS OF PEROXY RADICALS BY DUAL WAVELENGTH CAVITY RING-DOWN SPECTROSCOPY

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Organic peroxy radicals play important roles in combustion and atmospheric chemistry and selective monitoring of the abundance of these species in complex environment can provide vital information about the details of the relevant chemical processes. It has been demonstrated[a] that the $\tilde{A} \leftarrow \tilde{X}$ electronic transition observed in the near-IR region is a convenient spectroscopic marker that provides the required selectivity, however, knowledge of the absolute absorption cross-sections is required for the use of this technique to obtain absolute concentrations.

A novel apparatus for measuring of the absolute absorption cross-section of reactive species, such as organic peroxy radicals, is presented and characterized. The dual wavelength cavity ring-down setup (2-CRDS) utilizes simultaneous probing of the reaction region along equivalent optical paths at two different wavelengths. The absorption of the radicals of interest is measured along with that of well known byproduct species, whose absorption signal is used for determining the concentration of radicals. The proof of principle is demonstrated by the measurements of the absorption cross-section of $\tilde{A} \leftarrow \tilde{X}$ transition of both conformers of the ethyl peroxy radical, $C_2H_5O_2$. The radical production involves hydrogen abstraction by chlorine atoms from ethane forming ethyl radical, in which HCl is formed as a byproduct and used as a "reporter" molecule. The ethyl radicals subsequently rapidly attach to oxygen molecules to form ethyl peroxy radicals under our experimental conditions.

These measurements are compared to other methods for measuring absolute absorption cross-sections, such as measurements of the decay rates of the radical concentration due to self-reaction and measuring the photolysis beam absorption by oxalyl chloride, $(COCl)_2$ to determine chlorine atom production. The sources of systematic and random errors will be discussed.

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[a] E.Sharp, P.Rupper and T.A.Miller, *Phys. Chem. Chem. Phys.*, **10**, 3955, (2008)