QUANTITATIVE MEASUREMENTS OF ABSORPTION CROSS-SECTIONS BY DUAL WAVELENGTH CAVITY RING-DOWN SPECTROSCOPY

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The organic peroxy radicals play an important role in atmospheric and combustion chemistry and their absolute concentrations provide key data for understanding these processes. These concetrations can be measured by monitoring the absorption by these species. To do this, however, the absorption cross-section must be known. Data on the cross-sections of strong $\tilde{B} \leftarrow \tilde{X}$ peroxy transitions are abundant, but these transitions lack selectivity and their analytical use is limited. Recently, we reported observation and analysis of selective, but weak $\tilde{A} \leftarrow \tilde{X}$ spectra of a number of peroxy radicals that are quite selective. However, corresponding data on their absorption cross-section are scarse. Moreover, these cross-sections are hard to determine from even good quantum chemistry calculations.Cross-sections can be determined from observed fractional absorption if the concentration of the absorbing species is known. Determining concentrations of reactive intermediates is a challange which can be experimentally overcome by simultaneous observation of the absorption by the peroxy radical and by a co-product with well-known absorption properties (e.g., HCl). However, peroxy radicals and their co-product may absorb in very different frequency regions. To make such measurements we designed a dual wavelength CRDS system that allows probing the absorbing media along closely lying optical paths at different wavelengths at the same time. In this talk we will discuss the design of the novel apparatus and its capabilities and performance. As an example of an application, we present the measurement of the absolute absorption cross-section for the weakly absorbing $\tilde{A} \leftarrow \tilde{X}$ transition of reactive intermediate, ethyl peroxy radical.