

CONCENTRATION DETERMINATIONS FOR REACTIVE CHEMICAL INTERMEDIATES USING EMPIRICALLY DETERMINED AND THEORETICALLY CALCULATED TRANSITION PROBABILITIES

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It has long been recognized that the Beer-Lambert law allows the determination of molecular concentrations from experimentally measured transition intensities of absorption spectra provided the absorption cross section and path length are known, with the latter typically easily measured experimentally. For non-reactive molecules, a suitable standard of known concentration/pressure can provide the cross section if it is not already available from published molecular line lists. However, for many chemical intermediates, their reactivity precludes preparing such a standard and accounts for their frequent absence in molecular line lists. Nonetheless, such molecules play important roles in chemical reactions of significance both economically and environmentally; hence spectroscopic measurements of their concentrations can be very valuable. Historically such cross sections have been determined empirically by “on-the-fly” concentration measurements, mostly depending on the sometimes questionable assumption that the chemistry of these intermediates is thoroughly understood. For example, if the self-reaction rate constant of an isolated intermediate is accurately known, measurement of its temporal decay yields its concentration, thereby providing the line’s cross section from its intensity measurement. Alternatively, if a reaction mechanism is assumed that determines the stoichiometry of a reactive intermediate and a non-reactive byproduct with a known cross section, the measurement of their relative transition intensities provides the cross section of the intermediate. While such empirical cross sections have proven quite useful, it is worthwhile to note that it is also possible to calculate cross sections for individual rovibronic transitions using a combination of quantum chemistry methods and spectral simulation software. The peroxy radicals, RO₂ (R=H or alkyl group), are important intermediates in combustion and tropospheric chemistry with considerable work reported on their chemistry and spectroscopy. For the peroxy radicals, we compare results obtained from empirical cross sections measured by cavity ringdown spectroscopy with theoretically calculated values using the CFOUR quantum chemistry suite and the PGOPHER spectral simulation software.