CALCULATED AND EMPIRICAL VALUES OF VIBRONIC TRANSITION DIPOLE MOMENTS OF REACTIVE CHEMICAL INTERMEDIATES FOR DETERMINATION OF CONCENTRATIONS

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Absorption spectroscopy has long been known as a technique for making molecular concentration measurements and has received enhanced visibility in recent years with the advent of new techniques, like cavity ring-down spectroscopy, that have increased its sensitivity. To apply the method, it is necessary to have a known molecular absorption cross-section for the species of interest, which typically is obtained by measurements of a standard sample of known concentration. However, this method fails if the species is highly reactive, and indirect means for attaining the cross section must be employed. The HO_2 and alkyl peroxy radicals are examples of reactive species for which absorption cross-sections have been reported. This work explores and describes for these peroxy radicals the details of an alternative approach for obtaining these cross sections using quantum chemistry methods for the calculation of the transition dipole moment upon whose square the cross section depends. Likewise, details are given for obtaining the transition moment from the experimentally measured cross sections of individual rovibronic lines in the near-IR, $\tilde{A}$-$\tilde{X}$ electronic spectrum of HO_2 and the peaks of the rotational contours in the corresponding electronic transitions for the alkyl (methyl, ethyl, and acetyl) peroxy radicals. In the case of the alkyl peroxy radicals, good agreement for the transition moments, approximately 20%, is found between the two methods. However, rather surprisingly, the agreement is significantly poorer, approximately 40%, for the HO_2 radical. Possible reasons for this disagreement are discussed.