THE STRUCTURE AND SPECTRA OF ORGANIC PEROXY RADICALS

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Alkyl peroxy radicals ($C_nH_{2n+1}O_2$) are notoriously important reactive intermediates in the low-temperature combustion of hydrocarbons and in the chemistry of the atmosphere. These peroxy radicals have now been extensively studied via their $\tilde{A} - \tilde{X}$ electronic transition in the near-infrared with room-temperature cavity ringdown spectroscopy (CRDS). Last year, we presented our efforts to paint a big picture of these spectroscopic results, by combining the CRDS data of the first (methyl peroxy) through the fifth (pentyl peroxy) members of this homologous series to identify certain trends in the $\tilde{A} - \tilde{X}$ origin frequencies as a function of structure of the peroxy radical. Additionally, we were able to benchmark the quality of calculations for these systems by comparing experiment and theory for the C_1-C_5 alkyl peroxy radicals.

We present in this talk an extension of the work presented last year, where now detailed experimental spectral, structural relationships have been developed, which show the dependence of spectral properties on the number of carbon atoms in the radical, and its isomeric and conformeric structure. These relationships are explored and rationalized with the help of quantum chemistry calculations of the peroxy's orbitals involved in the $\tilde{A} - \tilde{X}$ electronic transition.