THEORETICAL INVESTIGATION OF LARGE AMPLITUDE TORSIONAL MOTION IN THE METHYL PEROXY RADICAL

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Organic peroxy radicals are key intermediates in the oxidation of hydrocarbons. The simplest organic peroxy radical, methyl peroxy CH_3O_2, is obviously the starting point for understanding the alkyl peroxies from both a theoretically and a spectroscopic point of view. The $\widetilde{A}-\widetilde{X}$ NIR electronic transition was first observed in 1976 by Hunziker. In 2000, our laboratory observed this transition using room temperature cavity ringdown spectroscopy (CRDS). In none of the previous reports has detailed consideration been given to the large amplitude torsional motion between the methyl top and O_2 moeity. In order to investigate this torsional mode, we computed the potential energy surface (PES) as a function of the OOCH torsion angle for both the $\widetilde{X}$ and $\widetilde{A}$ electronic states, minimizing the potential energy with respect to the remaining eleven internal coordinates. After fitting the calculated PES with an analytical form for the potential, we obtain the eigenvalues and eigenfunctions for the torsional motion and simulate the corresponding transition in the room temperature CRDS spectrum. The simulated spectra allowed us to understand the effect of the tunneling splitting associated with the torsional sequence bands and also allowed us to assign atypical spectral features associated with transitions from the free rotor regime of methyl peroxy.