ANALYSIS OF THE ROTATIONAL STRUCTURE OF $\tilde{B}^2A' \leftarrow \tilde{X}^2A'$ TRANSITION OF ISOPROPOXY RADICAL: ISOLATED STATE vs. COUPLED STATES MODEL

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Isopropoxy radicals are reactive intermediates in atmospheric and combustion chemistry. From the theoretical point of view, they represent an extreme case of "isotopically" substituted methoxy radicals with two methyl groups playing the role of heavy hydrogen isotopes. Previously[a] the rotationally resolved spectra of $\tilde{B}^2A' \leftarrow \tilde{X}^2A'$ electronic transition were successfully analyzed using a simple effective rotational Hamiltonian of the isolated $\tilde{X}$ and $\tilde{B}$ states. However, a number of the experimentally determined parameters appeared dramatically inconsistent with the quantum chemistry calculations and theoretical predictions based on the symmetry arguments.
Recently, we analyzed these spectra using a coupled two state model, which explicitly includes interactions between the ground $\tilde{X}^2A'$ state and low-lying excited $\tilde{A}^2A''$ state. In this presentation we will discuss the results of this analysis and compare the parameters of both models and their physical significance.

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[a] D. G. Melnik, T. A. Miller and J. Liu, **TI15**, *67th Molecular Spectroscopy Symposium*, Columbus, 2012