ROTATIONAL AND FINE STRUCTURE ANALYSES OF THE HIGH-RESOLUTION LIF SPECTRA OF THE DEUTERATED ISOTOPOMERS OF THE METHOXY RADICAL

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The methoxy radical, CH_3O, is one of the most interesting and most widely-studied free radicals. It provides a benchmark case of the Jahn-Teller effect in a molecule with spin-orbit interaction. The partial deuteration of the methoxy radical breaks the molecular symmetry, thereby reducing the electronic orbital angular momentum in the $\tilde{X}^2$E ground state by introducing new terms in the rovibronic Hamiltonian of CH_3O. The resolved rotational and fine structure in the LIF spectra of CHD_2O and CH_2DO has been assigned and analyzed by simulating and fitting the 3_0^2 and $(6')_0^1$ bands of the $\tilde{A}^2A_1$–$\tilde{X}^2E_{3/2}$ transition for each isotopomer, providing molecular constants and energy levels for both states of each isotopomer. The ground state results were used to predict the previously observed $\tilde{X}$ state microwave spectrum.[a] This prediction is consistent within the experimental accuracy of the LIF experiment. As an additional control, the 3_0^2 and 6_0^1 bands of the $\tilde{A}^2A_1$–$\tilde{X}^2E_{3/2}$ transition for CH_3O and CD_3O were analyzed using the same method.[b] Efforts are underway to fit simultaneously the LIF, microwave, and possibly SEP data of the ground state of these isotopomers to a rotational and fine structure Hamiltonian.

[a] D. Melnik, V. Stakhursky, V. A. Lozovsky, T. A. Miller, C. B. Moore and F. C. De Lucia, WJ09, 59^{th} International Symposium on Molecular Spectroscopy, 2004.

[b] Y. Endo, S. Saito and E. Hirota, *J. Chem. Phys.* **81**, 122 (1984).