ROVIBRONIC BANDS OF THE $\tilde{A} - \tilde{X}$ ELECTRONIC TRANSITION OF CH_3O_2 AND CD_3O_2 DETECTED WITH CAVITY RINGDOWN ABSORPTION IN THE NIR.

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Methyl peroxy (CH_3O_2) is the simplest alkyl peroxy radical. It is therefore the starting point for the subsequent investigation of larger alkyl peroxy radicals, which are key reaction intermediates in a variety of processes in atmospheric as well as in combustion chemistry. Its spectroscopic characterization is a prerequisite for monitoring its presence and concentration in order to understand as completely as possible the chemistry of gas phase reactions involving these reactive species. Several investigations of the spectrum of methyl peroxy have recently been reported[a,b].

We now report several rovibronic bands of CH_3O_2 and CD_3O_2 in their $\tilde{A}\,^2A'$ - $\tilde{X}\,^2A''$ electronic transitions in the range 1.22 - 1.40 μm with the cavity ringdown technique that have not been discussed in detail before. While the electronic origins and COO symmetric stretching modes for these two species have been reported previously, other rovibronic bands are described here for the first time. These bands include the COO bending modes as well as many hot bands involving the methyl torsional mode (ν_{12}). Both typical sequence structure and some atypical transitions involving ν_{12} have been observed. The latter ones are due to the location of the vibrational energy levels with respect to the relatively low, but quite different, barriers in the $\tilde{X}$ and $\tilde{A}$ states. The 12^2_2 band in CH_3O_2 and the 12^3_3 band in CD_3O_2 show quite different structures than the origin bands, an effect which results from tunneling splittings comparable to the rotational contour.

[a] M. B. Pushkarsky, S. J. Zalyubovsky and T. A. Miller *J. Chem. Phys.* **112**, 10695 (2000).
[b] C.-Y. Chung, C.-W. Cheng and Y.-P. Lee *The 61st Symposium on Molecular Spectroscopy*, 2006, RF02.