DISPERSED FLUORESCENCE SPECTROSCOPY OF PRIMARY AND SECONDARY ALKOXY RADICALS

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The oxidation of hydrocarbons is among the most important of chemical processes. Alkoxy radicals (RO) are key intermediates in combustion and in the degradation of volatile organic compounds injected into our atmosphere. The reactions of these simplest oxygen-containing organic radicals affects the yield of ozone, air toxics, and organic aerosols in the atmosphere. Hence elucidation of their chemistry is important for obtaining a better understanding of combustion and the impact of hydrocarbons in the atmosphere. Dispersed fluorescence spectra of 1-propoxy, 1-butoxy, 2-propoxy and 2-butoxy radicals have been observed under supersonic jet cooling conditions by pumping different vibronic bands of the $\widetilde{B}$-$\widetilde{X}$ laser induced fluorescence excitation spectrum. The DF spectra were recorded for both conformers of 1-propoxy, three conformers of the possible five of 1-butoxy, two conformers of the possible three of 2-butoxy and the one possible conformer of 2-propoxy. Analysis of the spectra yield vibrational frequencies for the ground $\widetilde{X}$ electronic state, and in some cases for the low-lying $\widetilde{A}$ electronic state as well as the energy separation of their vibrationless levels. In all cases, the vibrational structure of the DF spectra is dominated by a C-O stretch progression yielding the ν_{CO} stretching frequency for the $\widetilde{X}$ state and in some cases for the $\widetilde{A}$ state. In addition to the experimental work, quantum chemical calculations were carried out for some conformers to aid the assignment of the vibrational levels of the $\widetilde{X}$ state and the $\widetilde{A}$ state. Geometry optimizations of the different conformers of the isomers and determination of their energy difference in their ground state were performed. The results of the calculation of the energy separations of the close-lying $\widetilde{X}$ and $\widetilde{A}$ states of the different conformations are compared with the experimental observations.