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FLUORESCENCE LIFETIMES OF LASER-EXCITED ALKOXY RADICALS, P. MISRA, C. SANDIFOR, AND X. ZHU

Alkoxyl radicals play a leading role as oxidation intermediates in the combustion of hydrocarbons and in air pollution. The radicals were generated in a supersonic expansion by photofragmentation of alkynitrile precursors and subsequently excited by a frequency-doubled Nd:YAG-pumped dye laser. Fluorescence decay following excitation was displayed on the screen of a digital oscilloscope and stored for analysis. Fluorescence lifetime data involving the CO-stretch vibrational mode for excited vibrational quanta \( v^* = 0\) for methoxy, ethoxy and isoproxy were found to be in the range 0.15-3.00 \( \mu s \). Of the three transient species studied, isoproxy had the shortest lifetime, methoxy the longest, and ethoxy was intermediate between the two. For example, for two quanta excitation of CO-stretch, the lifetimes were 1.55 \( \mu s \) for methoxy, 0.98 \( \mu s \) for ethoxy and 0.62 \( \mu s \) for isoproxy. Time-resolved emission of ethoxy for the vibrronic band involving five quanta of CO-stretch excitation gave a considerably reduced lifetime of 0.14 \( \mu s \). All of the above-cited observations appear to point to the availability of important non-radiative decay channels for excited alkoxy radicals.

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SPECTROSCOPIC OBSERVATION OF THE ZnC\(_2\)H\(_4\) RADICAL

Andrew J. Beant, Gary K. Corlett, Ian M. Povey, Simon J. Pooley, and Andrew M. Ellis

Laser-induced fluorescence has been used to make the first spectroscopic observation of the zinc monomethyld radical. This radical has been produced in a supersonic jet using electrical discharge fragmentation of zinc diethyl. The A-X origin is significantly red-shifted from that of the related radical, zinc monomethyl,\(^1\) explaining why previous attempts to observe this molecule were unsuccessful.\(^2\) We have obtained both excitation and dispersed fluorescence spectra of ZnC\(_2\)H\(_4\), and will present an assignment of the vibrational structure in these spectra. In addition, we will describe how a pulsed electrical discharge can be used to synthesise metal-containing radicals such as ZnCH\(_3\) and ZnC\(_2\)H\(_3\) by direct reaction involving metal atoms.


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