TJ11 10 min 4:23

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

Alkoxy 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 alkylnitrite 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'=0-5 for methoxy, ethoxy and isopropoxy were found to be in the range 0.15-3.00 μs. Of the three transient species studied, isopropoxy 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 μs for methoxy, 0.98 μs for ethoxy and 0.62 μs for isopropoxy. Time-resolved emission of ethoxy for the vibronic band involving five quanta of CO-stretch excitation gave a considerably reduced lifetime of 0.14 μs. 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_2H_5 RADICAL

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Laser-induced fluorescence has been used to make the first spectroscopic observation of the zinc monoethyl radical. This radical has been produced in a supersonic jet using electrical discharge fragmentation of zinc diethyl. The $\tilde{A}$-$\tilde{X}$ 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_2H_5 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_2H_5 by direct reaction involving metal atoms.

[1]E. S. J. Robles, A. M. Ellis, and T. A. Miller, *Chem. Phys. Lett.* **178**, 185 (1991).
[2]R. L. Jackson, *J. Chem. Phys.* **96**, 5938 (1992).

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