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HIGH RESOLUTION, ROTATIONALLY RESOLVED ELECTRONIC SPECTRA OF CF₃S AND CF₃O

MIN-CHIEH YANG, DAVID E. POWERS, CHRISTOPHER C. CARTER, JAMES M. WILLIAMSON AND TERRY A. MILLER.

We have previously presented the high resolution rotationally resolved laser induced fluorescence excitation spectrum of the origin band of the $\tilde{A}^2A_1 \leftarrow \tilde{X}^2E$ electronic transition of CF₃O^a. We have now obtained rotationally resolved spectra for other vibrational bands of CF₃O. In addition, we have obtained similar electronic spectra involving several vibrational transitions of CF₃S. In both molecules, we observe excited vibrational states which are totally symmetric and ones of *e* symmetry, transitions to the latter probably being caused by the Jahn-Teller effect in the ground ²E state.

In CF₃O, the rotational structure of *e* - *e* vibronic transitions is much more congested than that of *a* - *e* vibronic transitions. This is because the allowed rotational transitions in the *e* - *e* bands are $|\Delta K| = 0$ and 1; while the allowed transitions of the *a* - *e* bands are $|\Delta K| = 1$. Nevertheless, the rotational structure of the *e* - *e* bands of CF₃S is less congested than that of the *a* - *e* bands. The rotational transitions of the *e* - *e* bands can be divided into several sub-groups with each sub-group containing a few rotational transitions and with the sub-groups separated by about 0.5 cm⁻¹. Overall rotational transitions of the *e* - *e* bands span $\gtrsim 6$ cm⁻¹. On the other hand, the rotational transitions of the *a* - *e* type bands of CF₃S span $\lesssim 4$ cm⁻¹.

^aX.-Q. Tan M.-C. Yang, C. C. Carter, J. M. Williamson, T. A. Miller, T. E. Mlsna, J. D. O. Anderson and D., D. Desmarreau, *J. Phys. Chem.* 98, 2732 (1994)

Min-Chieh Yang, David E. Powers, Christopher C. Carter, J. M. Williamson and T. A. Miller Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, OH 43210

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DETERMINATION OF SEVERAL NEW VIBRATIONAL FREQUENCIES FOR THE ETHOXY RADICAL,* P. MISRA, X. ZHU, AND M.M. KAMAL

The ethoxy molecule is an important chemical intermediate in combustion and atmospheric processes. It was formed by excimer laser-induced photolysis of ethylnitrite in a pulsed supersonic expansion. A frequency-doubled Nd:YAG-pumped dye laser in the UV with a nominal linewidth of 0.07 cm⁻¹ served as the probe beam for recording rotationally-resolved excitation spectra of the B-X system in the 310-344 nm region. Wavelength calibration was carried out using optogalvanic transitions employing an iron-neon lamp. In addition to the strong CO-stretch progression, several distinct excited state frequencies have been identified, namely: ν_4' (CH₂ scis)=1460 cm⁻¹, ν_7' (CH₂ wag)= 1323 cm⁻¹, ν_9' (CC stretch)= 869 cm⁻¹, ν_{10}' (CO stretch)= 603 cm⁻¹, ν_{11}' (CCO deform)= 362 cm⁻¹, ν_{17}' (CH₂ rock)= 893 cm⁻¹ and ν_{18}' (Torsion)= 244 cm⁻¹. Single vibronic level dispersed fluorescence spectra were recorded by exciting the molecules at the wavelength of a rotational transition within a vibronic band. Such dispersed spectra were obtained with an optical multichannel analyzer system used in conjunction with a cooled CCD detector. Besides the main CO-stretch progression in the wavelength-resolved emission spectra, there were other distinct ground state frequencies that could be identified and assigned: ν_2'' (CH₂ s-stretch)= 2753 cm⁻¹, ν_9'' (CC stretch)= 910 cm⁻¹, ν_{10}'' (CO stretch)= 1068 cm⁻¹, ν_{11}'' (CCO deform)= 444 cm⁻¹, ν_{15}'' (CH₂ twist)= 1277 cm⁻¹, ν_{16}'' (CH₃ rock)= 984 cm⁻¹, ν_{17}'' (CH₂ rock)= 943 cm⁻¹ and ν_{18}'' (torsion)= 370 cm⁻¹.

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Address of Misra, Zhu, and Kamal: Laser Spectroscopy Laboratory, Department of Physics and Astronomy, Howard University, Washington, D.C. 20059.