
Quantum Electronics and Laser Science Conference

1993 Technical Digest Series
Volume 12

Conference Edition

Summaries of papers presented at the
Quantum Electronics and Laser Science Conference
May 2-7, 1993
Baltimore, Maryland

Sponsored by
Optical Society of America
IEEE/Lasers and Electro-Optics Society
Laser Science Topical Group of the American Physical Society

in cooperation with
Quantum Electronics Division of the European Physical Society
Japanese Quantum Electronics Joint Group

Optical Society of America
2010 Massachusetts Avenue, NW
Washington, DC 20036-1023

was found to be at the same value of $z = 120$ as for the physical form of adsorption.

1. G. Betz and P. Varga, eds., *Desorption Induced by Electronic Transitions DIET 4*, (Austria, 1989).

QTuK48

Laser excitation spectroscopy of jet-cooled alkoxy and alkylthio radicals

P. Misra, X. Zhu, H. L. Bryant, R. Pai, A. H. Nur, M. M. Kamal, S. Alagudu, *Laser Spectroscopy Laboratory, Department of Physics and Astronomy, Howard University, Washington, D.C. 20059*

Alkoxy (RO; R = CH₃, C₂H₅, *i*-C₃H₇) radicals are important oxidation intermediates in air pollution, combustion phenomena, and astrophysical processes. The alkylthio (RS) radicals are chemical intermediates involved in natural sulfur emission in our atmosphere and contribute to acid precipitation. We have used the technique of laser-induced fluorescence (LIF) in conjunction with a supersonic jet expansion to record rotationally resolved excitation spectra of cold polyatomic RO and RS radicals.

The RO radicals were produced by fragmenting RONO, and the RS radicals were generated *in situ* in the jet by photodissociating R₂S₂. For both groups of precursors, the photolysis source was an excimer laser (KrF at 248 nm; Questek 2000). A YAG (Quanta Ray DCR11)-pumped tunable dye laser (PDL-2) was frequency doubled with a KDP crystal and, was used to probe the CH₃O and C₂H₅O radicals. A linewidth of 0.2 cm⁻¹ for the dye laser pulse could be narrowed to 0.05 cm⁻¹ by incorporating an étalon in the resonator cavity. For the *i*-C₃H₇O and RS radicals, the probe beam was an excimer (Questek 2030)-pumped tunable dye laser (PDL-3) with a pulse width of 0.07 cm⁻¹.

Several vibronic bands (3_0^0 , 2_0^1 , 2_0^2) of the $\tilde{A}^2A_1 - \tilde{X}^2E$ electronic system of CH₃O were recorded under low (0.2 cm⁻¹) and high (0.07 cm⁻¹) resolutions. The rotationally resolved excitation spectra were explicitly assigned by using the nomenclature for prolate symmetric-top transitions in spin-doublet states. A least-squares fit of the spectral data gave molecular parameters for both the excited and ground electronic states. Low-resolution excitation spectra of C₂H₅O were obtained for the $\tilde{A} - \tilde{X}9_0^0$ and 9_0^1 bands around 322.7 and 316.9 nm, respectively. A high-resolution spectrum of the 9_0^1 band of C₂H₅O was recorded in the 31552–31565-cm⁻¹ interval with a backing pressure of 250-psi (≈ 13 -k

Torr) helium. Several well-resolved $\tilde{A} - \tilde{X}$ vibronic bands of jet-cooled *i*-C₃H₇O were obtained in the 360–368 nm region.

Excitation scans for the $\tilde{A} - \tilde{X}$ system of CH₃S were recorded in the wavelength interval 357–387 nm and several vibronic bands involving the ν_2 (umbrella), ν_3 (C–S stretch), and ν_6 (rocking) vibrational modes were identified and assigned. A number of hot bands (with $\nu'' \neq 0$) in the 25 800–26 600-cm⁻¹ interval have been observed for the first time to our knowledge. A vibrational analysis of the $\tilde{A}^2A_1 - \tilde{X}^2E$ transitions yields the following values for the fundamental vibrations (to within 20 cm⁻¹) in the excited electronic state: $\nu_2' = 1085$ cm⁻¹, $\nu_3' = 401$ cm⁻¹, $\nu_6' = 1496$ cm⁻¹, and $\nu_6'' = 600$ cm⁻¹. Low-resolution excitation spectra of C₂H₅S were obtained in the 24600–25700-cm⁻¹ region, and a fairly strong band around 398.8 nm was recorded under high resolution. Rotationally resolved LIF spectra of the $\tilde{A} - \tilde{X}$ electronic system for *i*-C₃H₇S were obtained under similar conditions in the free jet in the 24300–25100-cm⁻¹ region. A detailed vibronic analysis of these jet-cooled spectra will be presented.

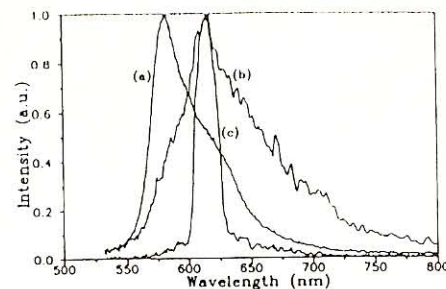
Financial support from the Center for the Study of Terrestrial and Extraterrestrial Atmospheres under National Aeronautics and Space Administration grant NAGW-2950, Wright Patterson Air Force Base under grant F33615-90-C-2038, and the Collaborative Core Unit of Howard University's Graduate School of Arts and Sciences is gratefully acknowledged.

QTuK49

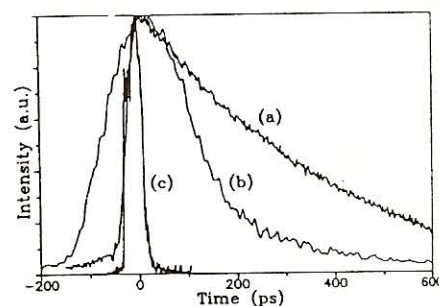
Time-resolved and excitation-dependent fluorescence of R-phycoerythrin crystals

Hezhou Wang, Xiguang Zheng, Fuli Zhao, Zhenxin Yu, Jinchang Zhu, Andong Xia, Lijin Jiang, *Institute for Lasers and Spectroscopy, Zhongshan (Sun Yat-sen) University, Guangzhou 510275, China*

Phycobiliproteins are important light-harvesting complexes and energy-transfer components in the photosynthetic systems of algae. Information about the structure and photophysical properties of C-phycoerythrin (C-PC) has been obtained by a crystallographic method and by time-resolved spectroscopic techniques, respectively. We have obtained single crystals of R-phycoerythrin (R-PE) from the marine red alga *Porphyridium urceolata* and have explored their time-resolved and excitation-dependent fluorescence spectra.



QTuK49 Fig. 1. Integrated fluorescences of R-PE crystals with different excitation photon densities: (a) 3×10^{12} , (b) 8×10^{15} , (c) 5×10^{16} photons/(cm² • pulse). Intensities are normalized to the maximum of each curve.



TuK49 Fig. 2. Emission decay curves of R-PE crystals with different excitation photon densities: (a) 3×10^{12} , (b) 8×10^{15} , (c) 5×10^{16} photons/(cm² • pulse). Intensities are normalized to the maximum of each curve.

Experiments were performed with the second harmonic of a mode-locked Nd:YAG laser as excitation source. The experimental results show that at low excitation photon density, the fluorescence of R-PE crystals peaks at 580 nm with a shoulder of weak emission at around 610 nm (see Fig. 1). This characteristic is similar to that for a dense solution. Either in dense solution or in crystals at low excitation intensity, the fluorescence at around 580 nm undergoes a rather long decay with a lifetime of several hundred picoseconds (see Fig. 2). With excitation density high enough, the duration of emission at 610 nm becomes shorter than that of the excitation laser and the intensity becomes much higher than that at 580 nm. The bandwidth of the novel sharp emission at 610 nm is approximately 11 nm at an excitation photon density of 10^{17} photons/(cm² • pulse).

The energy transfer in the crystals of R-PE is discussed. The excitation-density-dependent phenomena are proposed to