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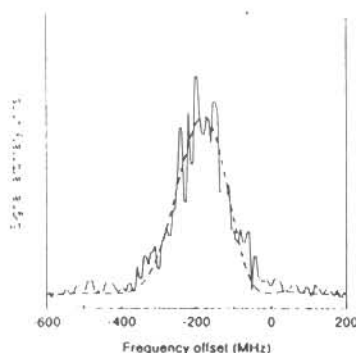
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QM2 Fig. 1. Measured (solid curve) and predicted (dashed curve) two-photon line shape of the $Q(0)$ transition in the $(0-0)$ band of the $ET \leftarrow X$ in D_2 . The frequency indicated on the x axis refers to the full VUV interval.

fractional accuracy is the best so far obtained for any measurement using pulsed lasers. The attainment of these high fractional accuracies presented a technical challenge. We have carefully designed both the dye amplifier chain to minimize frequency chirping and the optical lay-out so that the residual first-order Doppler shifts from angular misalignment can be compensated by the curvature of the Gaussian wave fronts.

This experiment, along with a future measurement of high molecular Rydberg states, will allow a determination of the ionization potential of molecular hydrogen, serving as one of the most sensitive tests of quantum electrodynamics in molecular systems.

This work was supported by the National Science Foundation.

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QM3 11:00 am

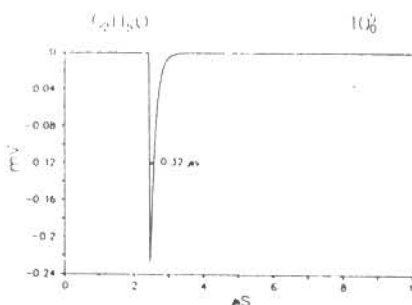
Fluorescence lifetimes of the alkoxy radicals

Xinming Zhu, Carron Sandifor, Mohammed M. Kamal, Prabhakar Misra, *Laser Spectroscopy Laboratory, Department of Physics and Astronomy, Howard University, Washington, D.C., 20059*

The alkoxy (RO; R = CH_3 , C_2H_5 , $i-C_3H_7$) radicals are important as oxidation intermediates in the combustion of hydrocarbons and in air pollution.¹ Alkyl nitrite (RONO) precursors (of typically 1–2% concentration) were transported by high-pressure helium (12–14 atm) and were supersonically expanded into a vacuum chamber through a commercial pulsed nozzle. The chamber pressure was $\sim 10^{-4}$ Torr with the pulsed valve in operation. UV radiation (typically 50-mJ pulses at 248 nm) was used to photodissociate RONO to generate the RO radicals *in situ* in the jet expansion.²



QM3 Fig. 1. Time-resolved emission recorded with a digital oscilloscope after laser excitation of the 0_0^1 band of ethoxy at 342.68 nm.



QM3 Fig. 2. Fluorescence decay of ethoxy after laser excitation of the 10_0^1 vibronic transition at 311.15 nm.

Tunable radiation from an Nd:YAG-pumped dye laser, which was frequency doubled to generate near-UV wavelengths, was used for exciting the ground-state radicals to the first excited electronic state. The probe UV-pulse energy was typically 100 μ J. Fluorescence emission after excitation was detected with a photomultiplier tube, and the corresponding decay curve was displayed on the screen of a digital oscilloscope. Lifetime measurements involving the CO stretch mode for the excited vibrational levels $v' = 0-5$ of CH_3O , C_2H_5O , and $i-C_3H_7O$ spanned the range 0.15–3 μ s. Methoxy (CH_3O) had the longest-lasting fluorescence, and isopropoxy ($i-C_3H_7O$) had the shortest, whereas ethoxy (C_2H_5O) had an intermediate lifetime. For example, for two-quanta excitation of the CO stretch, the lifetimes were 1.55 μ s for CH_3O and 0.62 μ s for $i-C_3H_7O$. For C_2H_5O , Fig. 1 shows the fluorescence-decay curve excited on the A–X (or B–X) 0_0^1 transition, yielding a lifetime of 0.94 μ s, and Fig. 2 depicts a trace of the time-resolved emission for the 10_0^1 vibronic band,³ indicating a considerably reduced lifetime of 0.32 μ s for the CO-stretch excitation. These observations are consistent with significant nonradiative decay routes being available in the excited states of the alkoxy radicals.

This work was supported by the U.S. Environmental Protection Agency's Office of Exploratory Research (R819720-01-0), NASA Lewis Research Center (NAG3-1677), and the Center for the Study of Terrestrial and Extraterrestrial Atmospheres (NASA NAGW-2950).

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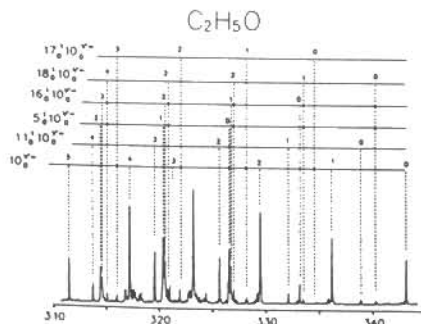
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Laser-induced fluorescence spectroscopy of the ethoxy radical in a supersonic jet expansion

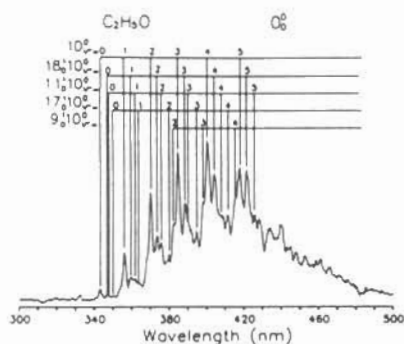
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The ethoxy (C_2H_5O) radical is an important chemical intermediate in combustion and atmospheric reactions.¹ It belongs to the C_2 point group and has 18 normal vibrational frequencies.² Four vibrational frequencies have been reported earlier,³ but only one—the CO stretch—has been assigned definitively. The C_2H_5O radical was generated *in situ* by photolyzing ethyl nitrite (C_2H_5ONO) with K₂F (at 248 nm) excimer-laser pulses. The nitrite precursor (at 1% concentration) was transported by helium under high pressure (12–14 atm) and was seeded into the vacuum chamber in the form of a supersonic molecular beam through a commercial pulsed nozzle. We have recorded laser-excitation spectra of jet-cooled C_2H_5O with 0.15- cm^{-1} resolution, and we have obtained dispersed fluorescence spectra with the aid of a 0.275-m monochromator (equipped with a 300-grooves/mm grating of 1-nm resolution). A frequency-doubled Nd:YAG-pumped dye laser with a nominal linewidth of 0.07 cm^{-1} served as the probe beam. Optogalvanic transitions excited by using a commercial F₂-N₂ hollow-cathode discharge lamp were used to calibrate the wavelength of the dye laser. The radicals were excited downstream in the jet expansion, and the delay between the photolysis and excitation beams was typically 8 μ s.

Laser excitation spectra of the A–X (or B–X) electronic system¹ of C_2H_5O were obtained in the spectra region 310–350 nm with rotationally resolved resolution. In addition to the main CO stretch progression shown in Fig. 1, there were seven other



QM4 Fig. 1. Laser-excitation spectrum of the ethoxy radical obtained in a supersonic jet expansion showing progressions involving the various vibrational modes ν_5 , ν_{10} , ν_{11} , ν_{16} , ν_{17} , and ν_{18} .



QM4 Fig. 2. Dispersed fluorescence spectrum of the ethoxy radical obtained when the 0_0^0 band was pumped. A 0.275-m-focal-length monochromator equipped with a 300-grooves/mm grating was used to record the spectrum; it provided a resolution of 1 nm.

distinct excited-state frequencies that could be identified, and these have been assigned² as follows: CO stretch ($\nu_{10} = 605 \text{ cm}^{-1}$), CC stretch ($\nu_4 = 895 \text{ cm}^{-1}$), CCO deform ($\nu_{11} = 365 \text{ cm}^{-1}$), CH_3 *d*-deform ($\nu_8' = 1472 \text{ cm}^{-1}$), CH_3 *s*-deform ($\nu_8'' = 1459 \text{ cm}^{-1}$), CH_3 rock (ν_{16} or $\nu_{16}'' = 871 \text{ cm}^{-1}$), CH_2 rock (ν_{17} or $\nu_{17}'' = 719 \text{ cm}^{-1}$), and torsion ($\nu_{18} = 245 \text{ cm}^{-1}$).

Dispersed fluorescence spectra of $\text{C}_2\text{H}_5\text{O}$ were recorded with an optical-multichannel-analyzer (OMA) system, and the wavelength calibration was carried out by using mercury lines. Seventeen bands excited in the near-UV provided strong emission and were dispersed with the OMA. Figure 2 shows a typical dispersed spectrum obtained by pumping the 0_0^0 band. To the best of our knowledge, 15 of the 17 bands are presented for the first time, together with detailed analysis of the structure of the wavelength-resolved emission spectra and the accompanying vibrational assignments.

This work was supported by the U.S. Environmental Protection Agency's Office of Exploratory Research (R819720-01-0), NASA Lewis Research Center (NAG3-1677), and the Center for the Study of Terrestrial and Extraterrestrial Atmospheres (NASA NAGW-2950).

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QM5 11:30 am

High-resolution spectroscopy of diatomic lithium

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We use various high-resolution laser-spectroscopy techniques to observe details in the spectrum of $^7\text{Li}_2$ that are otherwise unresolved. Perturbation-facilitated optical-

optical double-resonance (PFOODR) spectroscopy was used to access states in the triplet manifold. Optical-optical double-resonance (OODR) spectroscopy was used to detect Λ doubling. High-lying levels in singlet states were observed by using all-optical triple-resonance (AOTR) spectroscopy. Ionization detection greatly facilitated the observation of high-lying levels.

Molecular constants and RKR potential curves were obtained for the $2^3\Sigma_x^+$, $3^3\Sigma_x^+$, and $4^3\Sigma_x^+$ states. Our experimental T_e and R_e for the $2^3\Sigma_x^+$ state are $27297.45(16) \text{ cm}^{-1}$ and $3.0797(18) \text{ \AA}$, respectively, and for the $3^3\Sigma_x^+$ state they are $31043.93(53) \text{ cm}^{-1}$ and $3.0378(19) \text{ \AA}$, respectively. Hyperfine splitting for both states has been resolved. Both states follow a Hund's coupling case (b_{H}) hyperfine coupling scheme. The experimental Fermi contact parameter b_F is approximately $96.0 \pm 2 \text{ MHz}$ for the $2^3\Sigma_x^+$ state and $95.6 \pm 3 \text{ MHz}$ for the $3^3\Sigma_x^+$ state. These values are in good agreement with the previously obtained value of $98.6 \pm 4 \text{ MHz}$. One level of the $4^3\Sigma_x^+$ state has also been observed. Its hyperfine structure has been resolved and characterized with Hund's coupling case (b_{H}) as well.

Both e and f parity levels of the $G^1\Pi_x$ state have been observed. This enabled us to calculate a Λ -doubling parameter of $4.7220(49) \times 10^{-4}$. This is significantly less than the value extracted from previous experimental work.

High-lying levels in the $A^1\Sigma_u^+$, $F^1\Sigma_u^+$, and $G^1\Pi_x$ states have been observed. Detecting ions rather than collision-induced side fluorescence improved the signal-to-noise ratio by a factor of 20 in some cases. From these data we have calculated molecular constants for these states. We are also in the process of applying a new near-dissociation analysis that should lead to improved RKR potential curves.

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QM6 11:45 am

Large-dynamic-range spectroscopy of molecular relaxations

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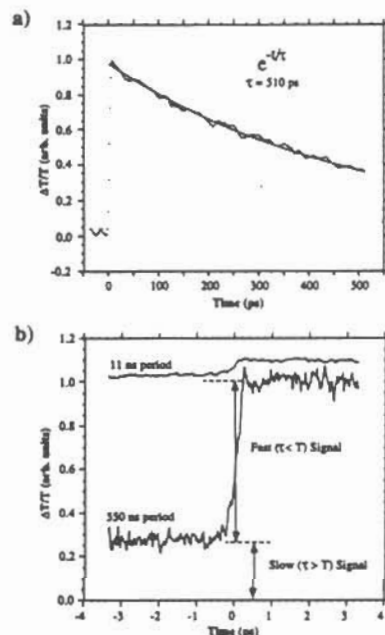
Over the last decade, time-resolved optical probes with subpicosecond temporal resolution have been used to directly measure fast relaxation processes in a wide variety of material systems. However, these techniques are impractical for measurements of relaxations occurring over several orders of magnitude in time. Relaxation processes that occur over many orders of magnitude in time are found in a wide variety of physical systems, including the excited-state dynamics of simple molecular systems and condensed matter systems, such as amorphous semiconductors and conductive polymers.

We have developed an experimental technique¹ that permits the measurement of relaxation processes with subpicosecond temporal resolution over a large temporal dynamic range of 10^7 , from $\sim 100 \text{ fs}$ to $> 1 \mu\text{s}$. The technique is applied to the mea-

surement of relaxation in organic-dye solutions to determine both the singlet and the much-longer triplet lifetimes in the same experiment.

The relaxation can be determined with subpicosecond resolution on short time scales (up to several nanoseconds) by mechanically varying the delay between the excitation and probe pulses. Slower relaxation processes are then mapped out in time by incrementally increasing the pulse repetition period external to the laser cavity by using a fast acousto-optic modulator. Using an unamplified CPM source and differential lock-in detection, we have measured signals with as few as one pulse in 1000 switched to the experiment, corresponding to $\sim 11 \mu\text{s}$ between pulses. Because this is an all-optical method, timing jitter is negligible on all time scales.

This technique is used to determine the complete $S_1-T_1-S_0$ relaxation dynamics of photoexcited organic-dye molecules in solution. In systems with small fluorescence quantum yield and fast intersystem crossing, the long-lived triplet state dominates relaxation dynamics. An example is the biological stain Azure A. Fast time-dependent processes are shown in Fig. 1(a), in-



QM6 Fig. 1. (a) Time-resolved relaxation of the excited singlet state of Azure A in ethylene glycol. The solid curve is a fit of exponential decay with $\tau = 510 \text{ ps}$. (b) Relative magnitude of the fast and slow time-varying signals for 11-ns (upper trace) and 550-ns (lower trace) laser repetition periods. Both traces have been normalized so that the peak value of the signal is unity, and the upper signal is offset by 0.1 for clarity. The magnitude of the time-dependent signals for both the 11-ns and the 550-ns repetition period is equal to within the noise level of the data. For an 11-ns repetition period the slow signal is ~ 15 times that of the time-dependent signal. For the 550-ns period the slow signal is reduced to half the magnitude of the time-dependent portion of the signal.