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Observation of Fluorescence Excitation Spectra of *tert*-Pentoxy and 3-Pentoxy Radicals†

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Fluorescence excitation spectra of *tert*-pentoxy [$CH_3CH_2C(O\bullet)(CH_3)_2$] and 3-pentoxy radicals were observed for the first time. The radicals were produced by laser photolysis of the corresponding pentyl nitrites at 355 nm and studied in the wavelength range 345−400 nm. For *tert*-pentoxy, 12 vibronic bands were labeled in three progressions. One dominant progression corresponds to the C−O stretch mode with initial vibrational interval 551 ± 10 cm^{-1}. Two other unknown mode progressions have vibrational intervals of 587 ± 10 and 631 ± 10 cm^{-1}. The transition origin was tentatively assigned at 25 491 ± 10 cm^{-1} (392.3 ± 0.1 nm). For 3-pentoxy, 15 vibronic bands were labeled in three progressions. The vibrational intervals in each progression are of consistent anharmonic tendency. On the basis of our assignments of the C−O stretch progression, the transition origin T_0, the C−O stretching vibration frequency ν_{C-O}, and the anharmonic constant χ_{C-O} are derived to be 26 437 ± 10, 578 ± 6, and −17 ± 2 cm^{-1}, respectively. The initial vibrational intervals of two other unknown modes are 596 ± 10 and 590 ± 10 cm^{-1}. The fluorescence lifetime of 3-pentoxy was determined to be about 150 ns. The short extent of the laser-induced fluorescence (LIF) excitation spectra of many C_2−C_5 alkoxy radicals is tentatively explained as arising from the opening of a predissociation channel at relatively low excitation energies. Results of efforts to obtain LIF excitation spectra for 10 additional large alkoxy radicals are reported.

I. Introduction

Alkoxy radicals play an important role in atmospheric chemistry. They are formed in high yields during the oxidation of most organic compounds.[1] The atmospheric chemistry of large alkoxy radicals ($\geq C_4$) is dominated by three main chemical reactions: decomposition, reaction with O_2, and isomerization;[2] and each reaction channel has different effects on the yield and distribution of ozone formed during a smog episode.[3] The absolute rate constants of these reactions are not generally known, and the absence of spectroscopic data has hindered progress on alkoxy radical kinetics. Fluorescence excitation spectra of small ($<C_4$) alkoxy radicals have long been known[4−10] and used for studies of reaction kinetics[6,11,12] Fluorescence excitation spectra of C_4 and larger alkoxy radicals, however, are limited to very recent publications on *tert*-butoxy and 2-butoxy.[13−16] These observations demonstrate that some large alkoxy radicals do fluoresce and motivate our investigation of the fluorescence behavior of other large alkoxy radicals.

Alkoxy radicals are also an interesting target in the field of photodissociation dynamics. The vinoxy radical (CH_2CHO), which is somewhat similar to alkoxy radicals, undergoes internal conversion (IC) even upon excitation of the origin band and also undergoes predissociation at higher energy.[17,18] By contrast, methoxy undergoes predissociation via coupling with repulsive states,[19−23] and there is no evidence for IC at lower energy.[24] Fluorescence lifetimes of alkoxy radicals vary significantly with size, from 2.6 μs in methoxy to ca. 100 ns in 2-butoxy radicals.[5,10,14,15,20,23,25−27] Finding a global explanation of this behavior is still a challenge.

In this paper, we report new laser-induced fluorescence (LIF) excitation spectra of *tert*-pentoxy and 3-pentoxy at 213 K. Preliminary analyses of the spectra are carried out, and some spectroscopic parameters are derived. In addition, we present and discuss our LIF observations of 10 additional large alkoxy radicals in the wavelength range 335−400 nm. Possible explanations for the fluorescence behavior of some C_2−C_5 alkoxy radicals are presented.

II. Experimental Section

The methodology and apparatus are basically the same as that presented in ref 14, so only a brief description is given here. Alkoxy radicals (1-butoxy, 2-methyl-1-propoxy, 1-pentoxy, 2-pentoxy, 3-pentoxy, 2-methyl-1-butoxy, 3-methyl-1-butoxy, *tert*-pentoxy, 3-methyl-2-butoxy, 3-methyl-3-pentoxy, benzyloxy, and cyclohexoxy) were generated by 355-nm laser photolysis of appropriate alkyl nitrites (RONO). Alkyl nitrites were synthesized by the dropwise addition of a solution of concentrated sulfuric acid and the corresponding alcohol to a saturated solution of $NaNO_2$.[28] The identity and purity of the nitrites was verified by measuring their FTIR,[29] UV,[30] and NMR[29] spectra.

The reaction cell consists of a Pyrex tube surrounded by a cooling jacket, which sets the experimental temperature at 213 K. Additional baffles have been added to the system detailed in ref 14 so as to reduce the laser scattering light: four cylindrical blackened Pyrex tubes (each 6 cm long and 2 cm o.d.) with a baffle attached to one end are connected together and located inside each arm of the cell. The gas mixture is composed of 2% RONO in N_2 or He. The mixture flows constantly through the reaction cell at a pressure of 6 Torr. On the basis of the RONO concentration, the photolysis energy,

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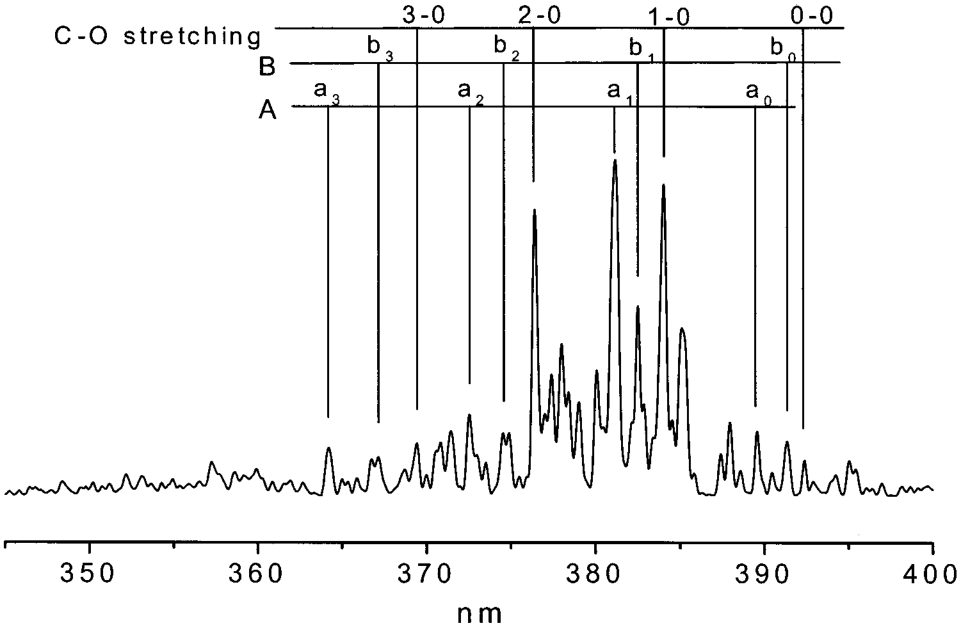

Figure 1. LIF excitation spectra of *tert*-pentoxy at 213 K. The sample comprises 2% *tert*-pentyl nitrite in N_2 at a total pressure of 6 torr. The delay time between the photolysis laser and the probe laser is 10 μs.

the shape of the laser beam, and the absorption cross sections, the initial radical concentration is estimated to be on the order of 1×10^{14} radicals cm^{-3}.

A frequency-tripled Nd:YAG laser (Quanta-Ray DCR-2) provides ~15 mJ/pulse at 355 nm for photolysis. The output of an excimer-pumped dye laser (Lambda Physik FL3002, 0.2 cm^{-1} line width) is about 1−2 mJ/pulse at 3.3 Hz. A tuning range of 335−400 nm is obtained by the use of three different dyes: PTP, DMQ, and PPI. The dye-laser wavelength is scanned at 0.04 nm s^{-1}. The photolysis and probe laser beams counterpropagate collinearly through the inner Pyrex tube. The delay time between the two lasers was fixed at 10 μs. The fluorescence signal is collected perpendicularly to the laser beams by a pair of lenses and focused on a photomultiplier tube (Hamamatsu R212). Two filters are used to reduce the scattered light.[14] The amplifier output is integrated by a boxcar averager. The excitation frequency is calibrated by the same procedure as in ref 14 to be 10 cm^{-1} larger than the true frequency. Spectral data are normalized by dividing the experimental spectral data by the background obtained by blocking the 355-nm photolysis laser. A 10−15-point smoothing process has been applied to the spectral data before they were plotted.

III. Results and Discussion

A. LIF Excitation Spectra of *tert*-Pentoxy and 3-Pentoxy. Figure 1 shows the LIF excitation spectrum of the *tert*-pentoxy $\tilde{B}-\tilde{X}$ transition[31] in the wavelength range 345−400 nm. Three progressions can be tentatively identified, each possessing four vibronic bands. By analogy to other alkoxy radical spectra, the dominant progression is assigned to the C−O stretching mode. The vibrational intervals in this progression decrease from 551 to 504 cm^{-1}. Although there is an identifiable anharmonic tendency, a reliable fit of the anharmonic constant cannot be obtained because there are only three intervals in each progression. The other dominant progression, with an initial vibrational interval of 631 cm^{-1}, is labeled as unknown progression A. Although the a_1 band in this progression is the strongest single peak in the spectrum, the vibrational interval is far greater than the 520−580 cm^{-1} found for the C−O stretch progression of C_2-C_4 alkoxy radicals.[14] Another weak progression with an initial vibrational interval of 587 cm^{-1} is labeled as unknown progression B. Bands in these two unknown progressions are labeled as a_0, a_1, a_2, ... and b_0, b_1, b_2, ..., respectively. Although some published alkoxy radical spectra show hot bands of the C−O stretching mode,[7] neither of these two unknown progressions can be assigned to progressions built on a hot band of the C−O stretching transition. It is known that the C−O stretching frequency of the electronic ground state for all alkoxy radicals is about 1000 cm^{-1},[4,7,10,32] and our B3LYP/6-31G(d) computation produces a value 962 cm^{-1} for *tert*-pentoxy.[33] However, the energy difference of 962 cm^{-1} is not found between the (0−0) band in the C−O stretching progression and the first member in progression A or B. Moreover, the modes labeled A and B must represent different progressions, because the vibrational intervals and band structures of these two progressions are obviously different. By analogy to the spectrum of methoxy radical,[7] a more reasonable guess is that these two unknown mode transitions originate from other combination excitations, but these cannot be identified from these spectra. Many additional peaks in Figure 1 cannot be attributed to well-established progressions and remain unlabeled. Those transitions occurring at longer wavelength than the assigned origin band are attributed to hot bands. All labeled band origins and their vibrational intervals are listed in Table 1. The transition origin was tentatively assigned to the band at 25 491 ± 10 cm^{-1} (392.3 ± 0.1 nm). The quoted uncertainty includes the reproducibility of the spectra and the breadth of the peak. The spectral shape and intensity are the same whether N_2 or He is used as a bath gas. The weakness of the signal has prevented us from accurately measuring fluorescence lifetimes.

Figure 2 shows the LIF excitation spectrum of the 3-pentoxy $\tilde{B}-\tilde{X}$ transition in the wavelength range 345−400 nm. No signals were found beyond this region. The overlapped part shows that spectra are repeatable. The spectroscopic analysis is similar to those of *tert*-pentoxy and all smaller alkoxy radicals.[6,9,10,14,34] Three progressions can be tentatively identified. One dominant progression is assigned to the C−O stretching mode with an initial vibrational interval 573 cm^{-1}. The upper-state vibrational level extends to $\nu'_{C-O} = 4$. Another dominant progression is labeled as unknown progression A with the initial

TABLE 1: Observed Band Origins of *tert*-Pentoxy $\tilde{B}-\tilde{X}$ (cm^{-1})

label	band origin ($\pm$10)	vibrational intervals ($\pm$10)
	C−O Stretching (v′−v″)	
0−0	25 491	
		551
1−0	26 042	
		525
2−0	26 567	
		504
3−0	27 071	
	Progression A	
a_0	25 602	
		631
a_1	26 233	
		613
a_2	26 846	
		611
a_3	27 457	
	Progression B	
b_0	25 553	
		587
b_1	26 140	
		555
b_2	26 695	
		546
b_3	27 241	

vibrational interval 596 cm^{-1}. Even though the strongest band lies in this progression, these transitions cannot be assigned to the C−O stretching mode. As discussed in the *tert*-pentoxy spectra, the vibrational interval in progression A is significantly larger than that of the C−O stretching progression. In addition, in most C_1-C_4 alkoxy radical spectra,[4−6,10,14] each band in the C−O stretching progression has a red shoulder, which can also be seen at peak 370.2 nm in the C−O stretching progression of the 3-pentoxy spectrum in Figure 2. Moreover, each strong band in unknown progression A, like those for other alkoxy radicals,[4−7,10,14,35] has a split to form a blue shoulder with ∼50 cm^{-1} spacing. The fairly consistent occurrence and position of such shoulders is unlikely to be accidental. Another weak progression is labeled as progression B with the initial vibrational interval 590 cm^{-1}. All bands in these two unknown mode progression are labeled as a_0, a_1, a_2, ...and b_0, b_1, b_2, ..., respectively. Although vibrational intervals in these two progressions are very close, the band features are distinctively different. These features can even be seen in the weak region (enlarged area in Figure 2). For instance, band a_4 has a split with spacing 34 cm^{-1} that band b_4 does not have.

All observed band origins with vibrational intervals are listed in Table 2. A definite anharmonic tendency can be seen in each progression. For the C−O stretching progression, eq 1 is used to fit the transition origin T_0, the C−O stretching frequency ν'_{C-O}, and the anharmonic constant χ'_{C-O}.[36]

$$T_{ev} = T_0 + \sum_i \nu^0_{C-O} v_i + \sum_i \sum_{k \geq i} \chi^0_{ik} v_i v_k + \cdots \qquad (1)$$

In eq 1, v_i and v_k are the upper-state vibrational quantum numbers corresponding to excitation modes *i* and *k*, respectively; in this situation, $k = i$, and $\nu^0_{C-O} = \nu'_{C-O} - \chi'_{C-O}$, because only the C−O stretching mode is excited. The derived T_0, ν'_{C-O}, and χ'_{C-O} values are 26 437 ± 5 (±10 with consideration of calibration uncertainty), 578 ± 6, and −17 ± 2 cm^{-1}, respectively. This anharmonicity χ'_{C-O} is larger than that of the C−O stretch mode ν''_3 of methoxy radical (reported as −8.4 or −4.64 cm^{-1}).[32,37] Because progressions A and B are probably from combination excitations with unknown mode assignments, no meaningful anharmonic constant can be determined.

Three stronger peaks (362.9, 370.2, and 375.5 nm) in Figure 2 are selected to measure fluorescence emission lifetimes. Zero-pressure fluorescence lifetimes for the three strongest bands of 3-pentoxy were obtained by extrapolating least-squares fits of lifetimes measured at total pressures of 1−10 Torr of the mixture of RONO in N_2. A typical fitting error is less than 3 ns on individual lifetime measurements and 10 ns on the extrapolated zero-pressure lifetimes. The resulting lifetimes of 140−160 ns for the three peaks are longer than those of 2-butoxy (ca. 85 ns) but close to that of *tert*-butoxy (ca. 150 ns).[14] Fluorescence intensity decreases sharply when the upper-state vibrational level of the C−O stretching mode is higher than $\nu'_{C-O} = 2$, but fluorescence does not cut off until at least $\nu'_{C-O} = 4$. We cannot reliably measure the fluorescence lifetimes of these weaker bands.

Let us consider the excited-state dynamics of the C_1-C_5 alkoxy radicals, and the potential consequences of these dynamics for LIF excitation spectra. In the case of methoxy, there is no evidence for dissociation upon excitation up to 35 436 cm^{-1} (about the band origin $\nu'_{C-O} = 6$). This appears to be the threshold for curve crossing to the directly dissociative $^4A_2$ state.[19,21−23] Excitation to $\nu'_{C-O} = 7$ leads to much faster predissociation, probably via more than one dissociative state.[19,23] As a result, the fluorescence excitation spectrum is unusually weak at $\nu'_{C-O} = 6$ and essentially absent by $\nu'_{C-O} = 8$.[20] Ethoxy radical shows strong LIF excitation spectra up to $\nu'_{C-O} = 5$.[5] Recent experiments by Choi, Bise, and Neumark[35] on ethoxy radical failed to find evidence for dissociation of the $\tilde{B}$ state; however, this was explained by low Franck−Condon factors for peaks with $\nu'_{C-O} > 5$. No conclusive study has been made of the $\tilde{B}$-state photodissociation dynamics of ethoxy or any larger alkoxy radical. In the following, we draw an analogy to methoxy to infer a possible explanation for the extent of the observed fluorescence excitation spectra.

Like ethoxy radical, 2-propoxy shows strong LIF excitation spectra up to $\nu'_{C-O} = 4$.[6,10] For 2-butoxy[14] and 3-pentoxy, the spectrum extends to $\nu'_{C-O} = 3$ and 4, respectively. For *tert*-butoxy[13,14,16] and *tert*-pentoxy, it extends to at least $\nu'_{C-O} = 7$ and 3, respectively. It is unreasonable to think that the *absorption* spectra of some of these alkoxy radicals have only 3−5 strong bands, whereas similar radicals have 7 or more bands. Therefore, we suggest that the short extent of the LIF excitation spectra of the larger alkoxy radicals is probably due to the opening of a channel that out-competes $\tilde{B}$ state emission. However, the recent work by Choi, Bise, and Neumark[38] noted that the highest excitation energy for which ethoxy radical fluoresces strongly is essentially isoenergetic with the C_2H_5 + O asymptote, whereas for methoxy, the corresponding excitation energy is ∼4700 cm^{-1} above the CH_3 + O asymptote. Therefore, they conclude that it is unlikely that ethoxy predissociates via C−O bond fission in the manner of methoxy. This result suggests the need to consider processes other than predissociation by C−O bond fission in the excited-state dynamics of larger alkoxy radicals as well.

For the related case of the vinoxy radical, it has been determined from fluorescence lifetimes and other data that the excited state undergoes internal conversion even at very low excitation energies.[17,18] This leads to dramatic changes in fluorescence lifetimes at energies well below the predissociation threshold. The fluorescence lifetime data for 3-pentoxy, 2-butoxy,[14] and *tert*-butoxy [14] do not exhibit nearly the same degree of variation with excitation energy (see, however, ref 15).

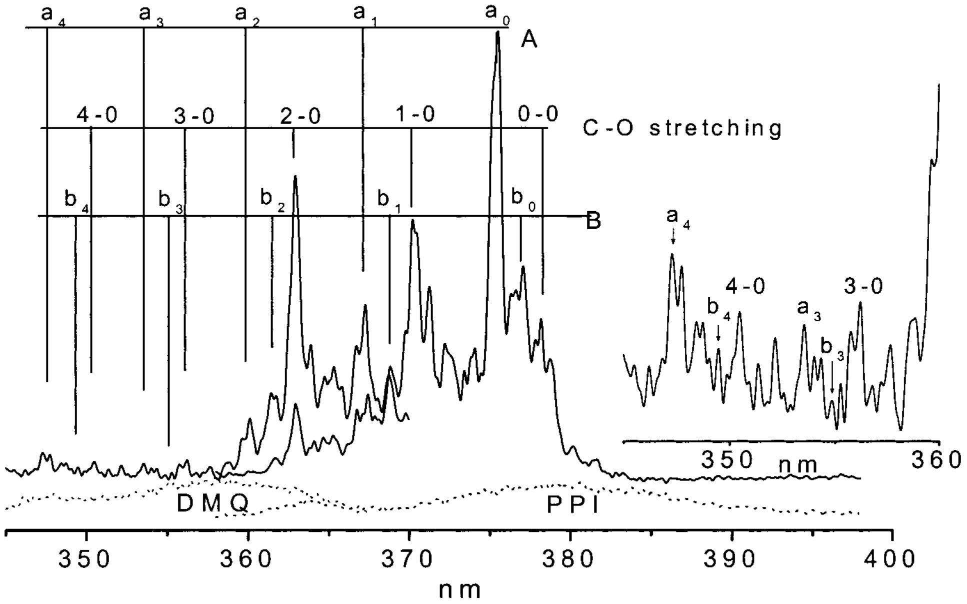

Figure 2. LIF excitation spectra of 3-pentoxy at 213 K. The sample comprises 2% 3-pentyl nitrite in N_2 at a total pressure of 6 torr. The delay time between the photolysis laser and the probe laser is 10 μs. Dots represent background spectra obtained in two different dyes (DMQ and PPI) by blocking the photolysis laser. The enlargement shows the spectra in the weak region (345−360 nm).

TABLE 2: Observed Band Origins of 3-Pentoxy $\tilde{B}-\tilde{X}$ (cm^{-1})

label	band origin (±10)	vibrational intervals (±10)
	C−O Stretching (v′−v″)	
0−0	26 439	
		573
1−0	27 012	
		544
2−0	27 556	
		515
3−0	28 074	
		465
4−0	28 539	
	Progression A	
a_0	26 631	
		596
a_1	27 227	
		542
a_2	27 769	
		512
a_3	28 281	
		479
a_4	28 760	
	Progression B	
b_0	26 525	
		590
b_1	27 115	
		548
b_2	27 663	
		490
b_3	28 153	
		463
b_4	28 616	

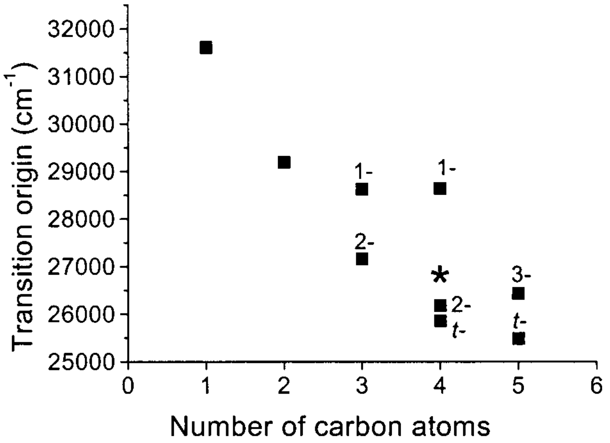

Figure 3. Transition origins of alkoxy radical versus alkoxy radical structure and number of carbon atoms in alkoxy radicals. Symbol 1, 2, 3, and *t* denote the isomeric form of the alkoxy radical. The values of transition origins of alkoxy radicals listed in the figure above are from refs 6−10, 25, 27, and 39 and this work. Symbol * denotes the suggested reassignment of the transition origin of 2-butoxy on the basis of the general tendency of transition origin, as discussed in the text.

B. LIF Observations of 14 Large Alkoxy Radicals. Knowledge of the general trend in the location of transition origins for alkoxy radicals studied to date will help us to predict the location of the origin band of other large alkoxy radicals. As shown in Figure 3, the transition origins of alkoxy radical UV spectra generally shift to lower energy with an increase in the number of carbon atoms. A much larger effect is seen upon going from primary to secondary and from secondary to tertiary alkoxy radicals. For instance, the transition origin shifts from 25 866 cm^{-1} in *tert*-butoxy[14,16] to 25 491 cm^{-1} in *tert*-pentoxy. 2-Butoxy would appear to be an exception, in that its transition origin was assigned[14] to a weak peak (26 185 cm^{-1}) at lower energy than that of 3-pentoxy (26 439 cm^{-1}). On the basis of the trend in Figure 3 and the tentative nature of the original assignment, it is more reasonable to assign the transition origin of 2-butoxy to the band labeled (1−0) (26 774 cm^{-1}) in ref 14. The conclusive assignment of transition origins will probably require analysis of jet-cooled spectra.

We have attempted to use LIF to investigate a total of 14 large alkoxy radicals in the range 335−400 nm. The results of all of our efforts are tabulated in Table 3. It can be seen that only 2-butoxy, 3-pentoxy, *tert*-butoxy, and *tert*-pentoxy fluoresce with *analyzable* band structure. Weak but extensively structured fluorescence excitation spectra were observed following photolysis of 2-pentylnitrite, 3-methyl-2-butylnitrite, and 3-methyl-3-pentylnitrite. Figure 4a shows a typical weak LIF excitation spectrum following photolysis of 3-methyl-3-pen-

TABLE 3: Review of LIF Observations Following Photolysis of Large Alkylnitrites in the Range 335−400 nm[a]

carbon	alkylnitrite	345−400 (nm)	360−400 (nm)	335−350 (nm)
4	1-butylnitrite		diffuse	$H_2C{=}O$ signal
	2-butylnitrite	RO signal		
	tert-butylnitrite	RO signal		
	2-methyl-1-propxylnitrite			$H_2C{=}O$ signal
5	1-pentylnitrite		diffuse	$H_2C{=}O$ signal
	2-pentylnitrite		weak signal	
	3-pentylnitrite	RO signal		
	2-methyl-1-butylnitrite		diffuse	$H_2C{=}O$ signal
	3-methyl-1-butylnitrite		no signal	
	tert-pentylnitrite (2-methyl-2-butylnitrite)	RO signal		
	3-methyl-2-butylnitrite		weak signal	
6	3-methyl-3-pentylnitrite		weak signal	
	cyclohexylnitrite		no signal	
other	benzylnitrite		no signal	

[a] "RO signal" means alkoxy radical signal with analyzable band structures. "Weak signal" means signals are very weak and have extensive structures, as in Figure 4a. "Diffuse" denotes the two broad bands with many small peaks on them, as in Figure 4b. "No signal" means neither diffuse signal, nor $H_2C{=}O$ signal, nor alkoxy radical signal. The wavelength range of 335−400 nm was obtained by using three different dyes: PTP, DMQ, and PPI.

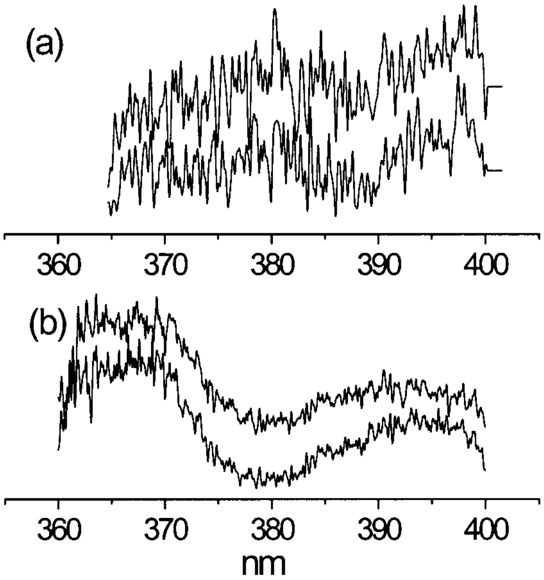

Figure 4. Fluorescence excitation spectra of uncertain origin, obtained following 355-nm photolysis of a 2% mixture of alkyl nitrite in N_2 at 213 K and a total pressure of 6 torr. The delay time between the photolysis laser and the probe laser is 10 μs. Two spectra were obtained in separate experiments with the same experimental conditions. (a) Following photolysis of 3-methyl-3-pentylnitrite, weak but highly structured spectra are observed. (b) Following photolysis of 1-butylnitrite, and probing at wavelengths far longer than the expected transition origin, diffuse spectra were observed.

tylnitrite; spectra of the three species were different but appeared to have some peaks in common. Although the spectrum is noisy, most of the strong peaks appear reproducibly.

We also attempted to investigate the primary alkoxy radicals 1-butoxy, 2-methyl-1-propoxy, 1-pentoxy, and 2-methyl-1-butoxy. In the range 335−350 nm, where primary alkoxy radicals are likely to absorb (see Figure 3 and ref 39), we observed an *identical* LIF excitation spectrum following photolysis of all four primary alkylnitrites. The same spectrum was obtained upon excitation of formaldehyde in the absence of the photolysis laser. Formation of formaldehyde from photolysis of primary alkylnitrites can be rationalized by the following scheme

$$\mathrm{RCH_2ONO} + h\nu \rightarrow \mathrm{RCH_2O}{\cdot}^{*} + \mathrm{NO}$$

$$\mathrm{RCH_2O}{\cdot}^{*} \rightarrow \mathrm{R}{\cdot} + \mathrm{CH_2{=}O}$$

(where * indicates vibrationally hot molecules). Note that, for most primary alkoxy radicals, the activation barrier to isomerization is thought to be significantly lower than that for decomposition,[1,2,40,41] but at sufficiently high internal energies, decomposition is favored because of its much higher Arrhenius *A* factor.[42] Maricq and Szente found a formaldehyde yield of only 16 ± 5% from the 351-nm photolysis of 1-butylnitrite at 295 K and 30 torr.[43] Very recently, Carter and co-workers observed the fluorescence excitation spectrum of 1-butoxy under jet-cooled conditions.[39] The apparent absence of fluorescence from primary alkoxy radicals in our experiments suggests that these radicals have undergone isomerization or decomposition to such an extent that the fluorescence from any radicals that do remain intact is obscured by the interference of the formaldehyde.

We also took fluorescence excitation spectra in the wavelength range 360−400 nm following photolysis of three of these primary alkyl nitrites (listed in Table 3); these wavelengths are far longer than the expected origin band of the $\tilde{B}$ state of primary alkoxy radicals (see Figure 3). For all three, we observed signal consisting of two broad diffuse bands. Figure 4b shows a typical spectrum of these large primary alkoxy radicals. No signal was observed following photolysis of 3-methyl-1-butylnitrite, benzylnitrite,[44] and cyclohexylnitrite in the wavelength range 360−400 nm.

We summarize here our observations of LIF excitation spectra of C_4 and larger alkoxy radicals: (1) Fluorescence spectra of four large alkoxy radicals—*tert*-butoxy, *tert*-pentoxy, 2-butoxy, and 3-pentoxy—have distinctive band structures. These observations suggest that under the supersonic jet conditions, one could obtain enough resolved structure to make mode assignments. It might also be possible to obtain rotationally resolved fluorescence spectra, which would enable determination of the precise transition origins and provide molecular structure data.[32,45] Furthermore, these excitation spectra can be used as a convenient tool for measuring absolute rate constants of chemical reactions relevant to these four large alkoxy radicals. (2) Fluorescence excitation spectra obtained following photolysis of 2-pentylnitrite, 3-methyl-2-butylnitrite, and 3-methyl-3-pentylnitrite are weak and exhibit many peaks but no dominant progressions; it is not clear that these signals arise from the corresponding alkoxy radicals. If they, in fact, do arise from alkoxy radicals, it will be a challenge to obtain analyzable LIF spectra for these alkoxy radicals. (3) At present, we have no explanation for the long-wavelength (360−400 nm) fluorescence observed following photolysis of large primary alkyl nitrites.

IV. Conclusion

LIF excitation spectra of *tert*-pentoxy and 3-pentoxy radicals were obtained in the wavelength range 345−400 nm; these are the first reported spectra of these species. The *tert*-pentoxy spectrum consists of many vibronic bands, of which 12 were assigned to three progressions. The initial vibrational interval of the C−O stretching mode is 551 ± 10 $\mathrm{cm^{-1}}$. The transition origin is tentatively assigned to the band at 25 491 ± 10 $\mathrm{cm^{-1}}$. The initial vibrational intervals of other two unknown modes are 587 ± 10 and 631 ± 10 $\mathrm{cm^{-1}}$. The excitation spectrum of 3-pentoxy also possesses many peaks; three extensive progressions consisting of 15 vibronic bands are labeled, and anharmonic parameters can be determined for the C−O stretch progression. The transition origin, the C−O stretching vibration frequency, and the anharmonic constant are derived to be 26 437 ± 10, 578 ± 6, and −17 ± 2 cm^{-1}, respectively, on the basis of our assignment of the C−O stretch progression. Two other unknown progressions have the initial vibrational intervals 596 ± 10 and 590 ± 10 cm^{-1}. The zero-pressure fluorescence lifetime of 3-pentoxy is determined to be 150 ± 10 ns. In addition, we reviewed our attempts to obtain LIF excitation spectra of 10 never-before studied alkoxy radicals. The results reported here should increase interest in photodissociation dynamics and high-resolution spectra of larger alkoxy radicals and assist those wishing to study the reaction kinetics of large alkoxy radicals.

Note Added in Proof. There is some disagreement about the location of the transition origin for *tert*-butoxy radical which affects the discussion of Figure 3. The "bulb" spectra of Wang, et al. (ref 14) and Lotz and Zellner (ref 16) agree, but jet-cooled spectrum of Carter, et al., (ref 39) suggests the origin band is the peak labeled (1-0) in the two bulb spectra. If the value of ref 39 is correct, then the effect of moving from a secondary to a tertiary radical may be rather small (merely ∼250 cm^{-1} instead of ∼900 cm^{-1} in the case of 2-butoxy vs *tert*-butoxy).

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