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Laser Excitation Spectra of Large Alkoxy Radicals Containing 5−12 Carbon Atoms

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Laser induced fluorescence spectra of nearly 20 jet-cooled alkoxy free radicals, with up to 12 carbon atoms, have been observed. Trends, as a function of the number of carbon atoms, are reported for origin frequencies, and their dependence upon structural isomers are documented. The interpretation of various bands in the spectra, and their rotational contours, in terms of excited-state vibrations and/or different conformations is discussed.

Introduction

The oxidation of hydrocarbons is a critically important chemical process. For example, it is the key chemical reaction in combustion chemistry, whether in stationary or mobile venues. It is also of great importance to atmospheric chemistry because hydrocarbons are injected via both natural and anthropogenic sources into the troposphere, where they subsequently undergo oxidation.

In the above processes, the chemistry is often complex and usually involves free radicals. The simplest such hydrocarbon oxidation products[1] are the alkoxy (RO) and peroxy (RO$_2$) radicals. This report will concern itself with the spectroscopic identification and characterization of the former species, the alkoxy radicals.

The electronic spectrum of the smallest saturated alkoxy radicals have long been studied, with numerous reports for methoxy[2−7] (CH$_3$O), ethoxy[8−12] (C$_2$H$_5$O), and 2-propoxy[13,14] (HC(O)(CH$_3$)$_2$). These works have established that the alkoxy radicals have a $\tilde{B}-\tilde{X}$ electronic transition in the near UV. The spectroscopy of this transition for the smaller alkoxy species is mostly well in hand, with full rotational and vibrational analysis available. (For the alkoxy radicals, there is a low-lying $\tilde{A}$ state, derived from the upper component of the degenerate $\tilde{X}^2$E state of methoxy, but it is not considered directly in the present studies.)

However, the spectroscopy of the larger alkoxy radicals has not been so well-developed, even though they have considerable practical importance because they result from the combustion of larger hydrocarbons found in fossil fuels or the atmospheric oxidation of larger organic species injected into the troposphere. For these reasons, there has been considerable recent interest in the larger species. There exist two recent reports[15,16] on the kinetics of the *t*-butoxy (*t*-C$_4$H$_9$O) radical. Dibble and co-workers have reported[17] laser induced fluorescence (LIF) studies at near ambient temperatures of *t*-butoxy as well as 2-butoxy (2-C$_4$H$_9$O) and most recently[18] *t*-pentoxy (*t*-C$_5$H$_{11}$O) and 3-pentoxy (3-C$_5$H$_{11}$O). In the recent near-ambient temperature work of Wang et al.,[18] LIF studies were attempted on 14 alkoxy isomers containing from four to six carbon atoms. Only the two butoxy and pentoxy isomers mentioned above were reported to give distinct, structured LIF spectra; the 10 other radicals were characterized as (i) giving weak signals (three radicals), (ii) diffuse spectra and/or signals from only formaldehyde (four radicals), or (iii) no signal (three radicals). The implication of the results is that these larger radicals do not have significant quantum yields for fluorescence from the $\tilde{B}$ state but rather decay by radiationless pathways, e.g., isomerization, fragmentation, or IVR. Such behavior is typical for nonradical molecular species of this size and larger.

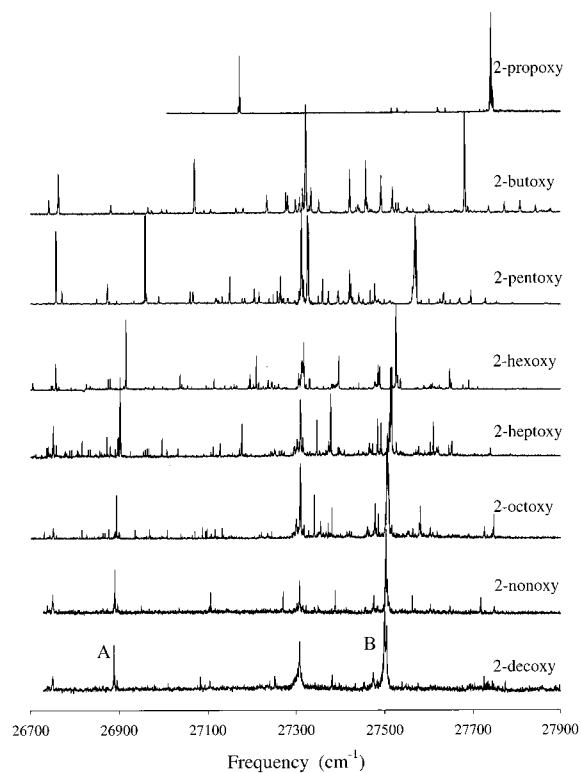On the basis of the renewed interest in the larger alkoxy
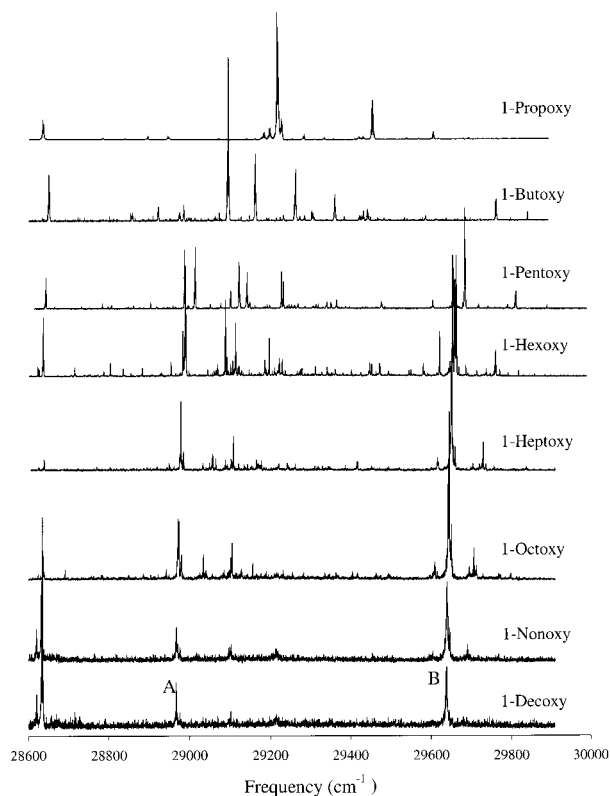
Figure 1. Survey scan of the LIF excitation spectra of the primary (1-) alkoxy radicals, $C_nH_{2n+1}O$, from $n = 3-10$. "Persistent" lines in the spectrum are marked A and B, see text for further details. Essentially no LIF signals are observed to frequencies higher than those shown.

Figure 2. Survey scan of the LIF excitation spectra of the secondary (2-) alkoxy radicals, $C_nH_{2n+1}O$, from $n = 3-10$. "Persistent" lines in the spectrum are marked A and B, see text for further details. Essentially no LIF signals, except for propoxy, are observed to frequencies higher than those shown.

radicals, we decided to investigate some of the alkoxy radicals cooled to free-jet temperatures and have recently reported LIF spectra[19] with nicely resolved vibrational structure for all of the isomers of propoxy and butoxy. Interestingly, the primary butoxy radical that had been reported to show only diffuse and/ or H_2CO fluorescence in the near ambient temperature work gave a sharp, structured LIF spectrum when jet-cooled.

Accordingly, we decided to survey a few of the larger alkoxy radicals to see if any of them had observable free-jet cooled LIF spectra. To our considerable surprise, under jet conditions, we have found sharp, structured LIF excitation spectra for about 20 alkoxy radicals containing from 5 to 12 carbon atoms, most of which have never been previously reported. In particular, we have systematically observed LIF spectra from all of the 1- and 2-alkoxy, $C_nH_{2n+1}O$, radicals with $n = 5$ through 10. We have also observed similar spectra for a number of other "randomly selected" isomers including 3-hexoxy, 4-heptoxy, 3-octoxy, 2,3 dimethyl-2-butoxy, 2,4-dimethyl-3-pentoxy, 4-methyl-3-heptoxy, and 3,6-dimethyl-4-heptoxy. In addition, the one alkoxy radical, 1-dodecoxy, with more than 10 carbon atoms that we investigated also showed a structured LIF spectrum. Indeed, by induction, we expect good quantum yields for $\tilde{B}$ state fluorescence for most any alkoxy radical produced from an alkyl hydrocarbon that would be found in common gasoline or diesel fuel or likely be injected into the troposphere. The remainder of this paper summarizes our observations and highlights some observed trends among the LIF spectra of the various radicals.

Experimental Section

All of the data were taken using a supersonic free-jet cooled expansion.[20-22] The experimental setup consisted of a XeCl (Lambda Physik EMG103) pumped dye laser (Questek PDL3),

with a line width of ~ 0.1 cm^{-1}, which was used as the probe laser to take the LIF data for all of the alkoxies. This work required the use of six laser dyes (PTP, DMQ, BBQ, PBBO, and Excalites 376 and 351). Photolysis of the precursor molecules was performed using a XeF (Lambda Physik Com-Pex110) excimer laser operating at 351 nm. Approximately 50 mJ/pulse of the XeF photolysis beam was focused just above the throat of the nozzle. This produced the desired alkoxy radical, which was then probed about 2 cm downstream. The total fluorescence was collected with a 1 in. f1 lens and imaged onto a photomultiplier tube (EMI QB9659). All data were calibrated using the lines of an Fe/Ne lamp.

The alkyl nitrite precursor molecules were produced by the dropwise addition of sulfuric acid to a mixture of the appropriate alcohol and sodium nitrate.[23] The alkyl nitrite precursor was kept in a sample bomb ranging in temperature from about -5 to $+25$ °C, depending on the precursor. A backing pressure of 100 psi of helium was passed over the sample, which was expanded into the chamber using a standard pulsed valve (General Valve) with a 500 μm orifice.

Results

As alluded to earlier, we have previously taken either moderate or high-resolution spectra of all of the alkoxy radicals, $C_nH_{2n+1}O$, with $n \leq 4$. We therefore decided to do a systematic survey of the primary (1-) and secondary (2-) alkoxy radicals with $n = 5-10$. The spectral results of that survey for the 1-alkoxy and 2-alkoxy radicals are shown in Figures 1 and 2, respectively, along with the previously reported spectra for the corresponding radicals with $n = 3$ and 4.

There are a number of interesting points about the alkoxy spectra illustrated in Figures 1 and 2. First, as can be seen by

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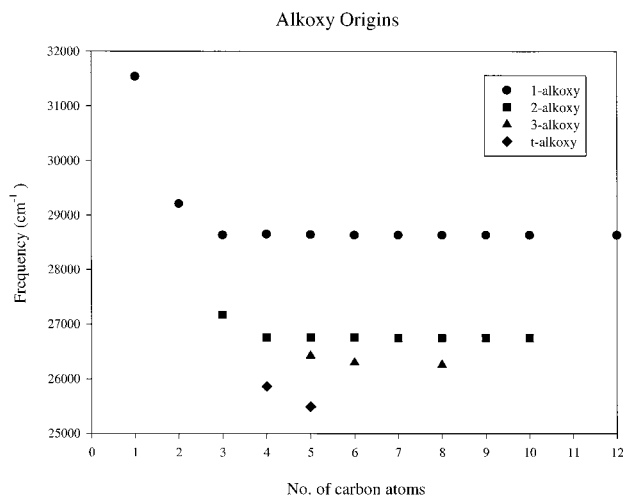
Figure 3. Frequencies of apparent origin bands of the observed alkoxy radicals plotted vs number of carbon atoms in the radical. The grouping of the radicals into families based on the nature of the isomer is clearly apparent.

Figure 4. Moderately high resolution ($\approx$0.1 cm^{-1}) scans over the region of the apparent origin bands of the 2-alkoxy radicals. Some rotational structure is apparent even for the largest radicals.

the figures, the spectra of all of these alkoxy radicals exhibit sharp LIF excitation spectra with well characterized vibrational structure. The S/N ratio becomes somewhat poorer as n increases but not dramatically so. No detailed studies of the fluorescence lifetimes have yet been performed, but qualitative observations indicate for the largest radicals a lifetime decrease of a factor of $\lesssim$5 from that of methoxy (2.2 μs). It appears that probably the most significant factor contributing to the observed decrease in S/N is simply a reduction in the vapor pressure for the higher molecular weight precursors, all of which were contained in a room-temperature reservoir.

In Figure 3, we have plotted the observed apparent origin frequency vs the number of carbon atoms for all of the observed alkoxy radicals from methoxy ($n = 1$) to dodecoxy ($n = 12$). (We use the term apparent origin to recognize the fact that it is the lowest frequency observed band of the spectrum; however, we cannot completely rule out the possibility of lower frequency members of a progression that were unobservable because of poor Franck–Condon factors and/or multiple origins corresponding to different conformers, etc.) Figure 3 shows that as the number of carbon atoms increases the apparent origin shifts to the red. However, it quickly reaches a nearly limiting value (higher resolution scans, see below, do indicate a small but continuing red shift with increasing n). Perhaps even more interesting is that the origin frequencies fall into distinct families defined by the branching of the alkyl chain. For a given value of n, the primary 1-alkoxies have the highest frequency origin with it decreasing monotonically for the 2 and 3 secondary isomers, with the tertiary isomers having the lowest frequency origin. The miscellaneous, branched compounds, e.g., the dimethyls, seemed to show a less systematic behavior, but generally speaking, these radicals appear to have lower frequency origins than the corresponding primary or secondary straight chain alkoxy radicals.

Figure 4 shows the apparent origin region of the 2-alkoxy radical LIF spectra with much better resolution. First one should notice that, although in Figure 3 the origin frequency appears to reach a limiting value around butoxy or pentoxy, Figure 4 shows that it continues to shift to the red as the number of carbon atoms increase. Although we plan higher resolution experiments in the future, the experimental resolution presently is limited by the laser bandwidth of about 0.1 cm^{-1}. Nonetheless, at least
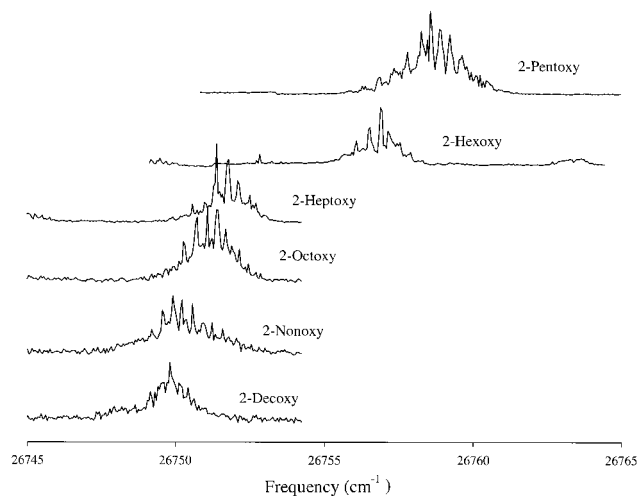
a partially resolved rotational structure is present in the origin band of all of the alkoxy radicals as shown in Figure 4.

Interestingly, the spectra in Figure 1 show little or no obvious hot band structure. This along with the relatively narrow rotational contour observed in Figure 1 indicates that the radicals are quite cold, both rotationally and vibrationally. The absence of hot bands does not characterize all of the larger alkoxy spectra that we have observed. However, Figure 1 demonstrates that under optimum conditions quite cold spectra can be obtained.

It is also worthwhile commenting on the vibrational structure of the 1- and 2-alkoxy radicals shown respectively in Figures 1 and 2. For the smaller species, the structure is quite complex, similar to that previously observed for the isomers of propoxy and butoxy. However, in the larger alkoxy radicals, the vibrational spectrum appears to considerably simplify, reducing to only two or three significant lines in the first 1000 cm^{-1} above the origin. Some of the effect may be attributed to a reduced S/N for the spectra of the larger alkoxies. However, it does not appear that this is by any means the complete explanation.

Our present observations are preliminary, and further data needs to be taken to substantiate them. However, presently observed spectral trends appear to be accounted for by a model which assumes that only a very small fraction of the possible vibrational fundamentals have significant Franck–Condon factors and hence significant oscillator strengths. However, even the smallest alkoxies depicted in Figures 1 and 2 have a significant number of low frequency modes with combinations and overtones in the region where the fundamentals with significant oscillator strength occur. In these smaller alkoxies, coupling between the vibrational levels appears to occur with concomitant intensity borrowing. However, as the radical increases in size, the efficiency of the borrowing seems to decrease with a smaller number of levels "lighting up". Indeed, for the largest alkoxy radicals, the spectra seem, at first approximation, to only exhibit the modes originally carrying the oscillator strength or levels very close to them as there is some evidence of line broadening in the lines of the vibrational excitations, compared to the origin. We anticipate carrying out a number of additional experiments to help clarify the situation.

It is inviting to speculate on the nature of the modes carrying the oscillator strength. Because of the large change in C–O bond length in the $\tilde{B}$–$\tilde{X}$ excitation, the smaller alkoxy radicals, i.e., methoxy, ethoxy, etc., are dominated by a progression in

the C—O stretch. In the spectra of the 2-alkoxies shown in Figure 2, there is a strong and persistent band between 550–560 cm^{-1} above the origin that we ascribe to the C—O stretch fundamental. Rather remarkably there is no clear analogue to this band (except for propoxy) in the spectra of the 1-alkoxies in Figure 1. A similar phenomenon has already been reported[19] in the spectrum of 1-butoxy. The explanation for the disappearance of the C—O fundamental is not clear. However, it appears from Figure 1 that in the 1-alkoxies the C—O stretch oscillator strength is shared among a large number of bands.

Besides the C—O fundamental there appears to be a couple of bands (marked A and B in the figures) which are persistent. They are at lower frequency in the 2-alkoxies than in the 1-alkoxies (approximate large *n* limiting values of 140 and 330 cm^{-1} relative to the apparent origin for A and 750 and 1000 cm^{-1} for B). It is inviting to associate these bands with a carbon–oxygen bending and C—C stretch motion, respectively. However, it could as easily be that the apparent origin belongs to one conformer and band A is the origin of a different conformer of the radical "frozen out" in the cold jet, with band B then being a vibration of the latter conformer. The latter explanation indeed appears supported by rather different rotational contours for the apparent origin and band A. We are at present performing further experiments and ab initio calculations to see if either of these speculations is correct.

Conclusions

In conclusion, we have observed, mostly for the first time, the LIF excitation spectra of nearly 20 large alkoxy radicals containing 5–12 carbon atoms. On the basis of these observations, we expect that most if not all comparably sized saturated aliphatic alkoxy radicals will have good quantum yields for fluorescence from the $\tilde{B}$ state. The spectra are all sharp, showing vibrational structure and even partially resolved rotational structure.

The apparent origin frequencies of similar alkoxy radicals shift to the red as the number of carbon atoms increase but vary quite slowly after reaching five or six carbon atoms. The origin frequencies fall into distinct groups on the basis of the nature of the isomer. The vibrational structure of the species actually appears to simplify with increasing chain length, with the spectra for the largest alkoxy radicals showing only a small number of "persistent" lines.

Having demonstrated LIF spectra of these large alkoxy radicals are possible, we anticipate future work characterizing these species in considerable detail. Much higher resolution spectroscopy is possible, hopefully permitting detailed rotational analysis for at least some of these species. Lifetime measurements can be undertaken to quantify their radiative properties and apparent near lack of nonradiative decay. Further experi-

ments, e.g., fluorescence depletion spectroscopy and ab initio calculations, may clarify the nature of the "persistent" lines and distinguish vibrational excitations from lines from different conformers. Once a fuller understanding of their spectroscopy and dynamics is obtained, detailed consideration of developing laser diagnostics for these larger alkoxy radicals can be undertaken.

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