

**Jet-cooled Laser-Induced-Fluorescence
Spectroscopy of Some Moderately
Large Alkoxy Radicals**

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Introduction

Much can be learned about molecules by observing how they interact with light. This field of chemistry/physics is termed spectroscopy. The Miller group focuses its attention on the spectroscopy of transient (short-lived) species. An interesting set of transient species is the alkoxy radicals, of the form RO, where R is an alkyl group. These species are thought to play a role as intermediates in the oxidation of hydrocarbons, both in atmospheric and combustion reactions¹⁻³. The methoxy and ethoxy radicals^{4,5} ($\text{CH}_3\text{O}^\bullet$ and $\text{CH}_3\text{CH}_2\text{O}^\bullet$, respectively) were studied quite extensively years ago. These spectra, as well as all of the other alkoxy spectra obtained in the Miller group, are obtained in a jet expansion. This cools the molecules to a few degrees above absolute zero. Because of the low temperature, practically all of the molecules will be in both the ground electronic and ground vibrational states prior to excitation with the laser. The peaks in the spectra that we see correspond to vibrational structure in an excited electronic state of the alkoxy. This structure can be fairly complex due to the fairly large number of vibrational modes in the alkoxyes.

Because of their significant role as chemical intermediates, spectroscopic interest in the alkoxy radicals has recently been renewed and has focused upon larger species. A number of spectra have been obtained for several propoxy, butoxy, and pentoxy isomers by others⁶⁻⁹. However, these were all performed at or near room temperature, and thus have very large linewidths due to the large number of rotational levels populated. Room temperature spectra also tend to contain vibrational hot bands, which are peaks in the spectra which result from a molecule being excited from higher vibrational levels in the ground electronic state. Hot bands make the analysis of the spectrum more difficult. Very recently we submitted a paper containing the first jet-cooled spectra of 2 propoxy and 3 butoxy isomers¹⁰ (see Figure 1 for alkoxy structures). We were able to make a number of assignments of the different vibrational modes in these spectra using *ab initio* calculations and also analogies between the larger and smaller alkoxyes.

All of the alkoxyes may be regarded as substituted versions of methoxy (CH_3O),

which with C_{3v} symmetry has a degenerate ground state. The A state of methoxy lies in the near UV, and is the one which is probed with LIF (laser-induced-fluorescence). The larger alkoxyes are less symmetric, and so the X state of methoxy splits into a ground state (designated X) and a low-lying excited state (designated A). The LIF experiments on the larger alkoxyes are still carried out on the UV transition analogous to the one in methoxy, but are now designated B-X.

The goal for the summer was to obtain jet-cooled spectra for even larger alkoxyes (number of carbons greater than 4), starting with the pentoxy isomers (see Figure 1), and then moving on from there.

Experimental

See Figure 2 for a schematic diagram of the experimental setup. The alkoxy radicals in these experiments were created from the corresponding alkyl nitrite precursors (of the form RONO) via photolysis. The synthesis of the alkyl nitrites, which are not commercially available, may be outlined as follows: H_2SO_4 was added dropwise to a flask containing ROH, H_2O , and $NaNO_2$. RONO was produced in the flask and was separated by distillation.

All the data were taken using a supersonic free-jet cooled expansion. The nitrite was placed in a sample bomb kept at a cold temperature for the experiment. Helium carrier gas (~100 psi) passed over the nitrite in the sample bomb on the way to the jet. The nitrite is kept at a temperature so that the vapor pressure is between 1 and 100 torr. The vapor above the liquid sample is what passes through the jet and is detected. Species in the jet move at a rate of about 2 mm/?s. The chamber into which the jet is expanding is at a pressure of $\sim 10^{-4}$ torr for these experiments. This low pressure is necessary in order to increase the mean free path of the molecules in the jet. The jet, and all of the lasers in this experiment are pulsed (usually 20 Hz). The photolysis reaction (RONO + $h\nu$ --> RO + NO) is carried out with an excimer laser (Lambda Physik ComPex110) which probes directly above the nozzle opening. Photolysis of the precursor

molecules was performed using XeF operating at 351 nm. Photolysis was attempted using ArF (193 nm) and KrF (248 nm), however this resulted in less alkoxy production. An excimer-pumped tunable dye laser (Questek PDL3) probes about 2 centimeters downstream of the photolysis laser and runs antiparallel to it. This “moderate resolution” dye laser has a linewidth of about 0.1 cm^{-1} . The data taken this summer used 3 different laser dyes: BBQ, DMQ, and p-terphenyl. There is a 400 to 500 ns delay between the opening of the pulse valve and the photolysis laser trigger and another delay of about 10 ns between the photolysis laser pulse and the dye laser pulse. The pulse width of all the lasers used in this experiment is on the order of 10 ns. The photomultiplier tube perpendicular to the two laser beams detects when there is fluorescence resulting from excitation of the alkoxy due to the dye laser. This signal is sent to a boxcar for signal averaging (and visualized on an oscilloscope), amplified, and is then sent to a computer for plotting. The data were calibrated using the lines of an Fe/Ne lamp.

Results

Figure 3 shows the jet-cooled spectrum that we have obtained for 1-pentoxy. Because of the jet’s cooling effect, nearly all of the alkoxy molecules which are produced are in the vibrationless level ($v=0$) in the ground electronic state. Thus, the first peak that we should see (the one of the lowest frequency) should correspond to a transition ending on the vibrationless level in the excited electronic state. This peak in the spectrum is called the “origin”. The peak in the 1-pentoxy spectrum around 28375 cm^{-1} is probably the origin. The additional peaks in this spectrum correspond to vibrational structure in the excited electronic state of 1-pentoxy. Since this is a fairly large polyatomic molecule (with $3 \times 17 - 6 = 45$ normal modes of vibration), this is a complicated spectrum. There are some typical vibrational modes that we expect to see in all of these alkoxy spectra, and they tend have characteristic vibrational frequencies (we know this from *ab initio* calculations on some of the smaller alkoxyes). Some of these are: methyl torsions ($\sim 300 \text{ cm}^{-1}$), backbone bends ($\sim 350 \text{ cm}^{-1}$), C-C-O deformations ($\sim 400 \text{ cm}^{-1}$), C-O

stretch ($\sim 550\text{ cm}^{-1}$), and C-C stretches ($\sim 800\text{ cm}^{-1}$). We haven't really been able to make many assignments for these modes in the spectra that we've obtained this summer; this will have to wait until the *ab initio* calculations are completed. For the propoxy and butoxy isomers, the C-O stretch bands were always found to be the strongest in the spectra¹⁰. This doesn't seem to hold for larger alkoxyes. The 1-pentoxy spectrum dies out around 29500 cm^{-1} . This is most likely due to the molecule dissociating before it fluoresces when it is highly excited vibrationally. The larger alkoxy spectra generally span a shorter frequency range than their smaller counterparts. Spectra for 3 more pentoxy isomers (2-pentoxy, 3-pentoxy, and 2-methyl-2-butoxy) are shown in Figures 4-6, respectively. The broad hump in Figure 6 is due to the dye laser curve (its power is a function of frequency), because the light scattered from the dye laser happened to be inside our boxcar gate while taking this spectrum.

Figures 7-10 show spectra that we have obtained this summer for 4 hexoxy isomers (1-hexoxy, 2-hexoxy, 3-hexoxy, and 2,3-dimethyl-2-butoxy, respectively). One thing to note is that the primary isomer (1-hexoxy, it is primary because the carbon bonded to the oxygen is only bonded to one other carbon) has an origin frequency shifted significantly to the blue (higher frequency), compared to the other hexoxy isomers. In addition, when one compares Figures 9 and 10, it becomes obvious that some isomers fluoresce more strongly than others. Figures 11 and 12 show spectra that we have collected from 2 heptoxy isomers (2-heptoxy and 4-heptoxy, respectively). Comparisons among the different sized alkoxyes indicate that the length of the LIF spectrum and the strength of the fluorescence signal have generally decreased with increasing size of the alkoxy (both features are also isomer-dependent).

Figures 13 and 14 show octoxy isomer spectra (3-octoxy and 4-methyl-3-heptoxy, respectively). Obtaining fluorescence from the octoxyes is particularly significant, since they are believed to be intermediates in the combustion of gasoline (which to a first approximation is octane). The octoxy spectra are quite dense in terms of peaks, with substantial overlap between bands. This is due in large part to many more vibrational

modes than in the smaller alkoxyes. Another complication in these spectra may be the existence of rotamers. Rotamers are spectroscopically distinct species, however they have the same formula, and unlike isomers, they even have the same connections between the atoms. They differ in their conformation, i.e. in their equilibrium geometry. With these large molecules, there can be many different geometries which can give nearly the same energy, and in this case, spectra can be seen from all of the different conformations, since all conformations will be present in the jet. Rotamers will tend to have a very similar energy level structure as one another, and so peaks corresponding to different rotamers will lie in the same region. This possibility makes the octoxy spectra very difficult to analyze. *Ab initio* calculations may be of some help, but it is doubtful that these spectra will ever be analyzed in their entirety.

Figure 15 summarizes all of the observed alkoxy origins that the Miller group has found. First it should be noted that the confidence in the assigned origin decreases as the number of carbons increases, because of the increase in complexity of the spectra. Some of the assigned origins may be “hot bands”. A hot band results when the alkoxy is not completely cooled in the jet and so some of the molecules are not in the $v=0$ level in the ground state. This is an unwanted occurrence and so in the past we have added a teflon vibrational cooling fixture on top of the nozzle. This fixture was shown in the past to cool methoxy⁴ and 2-butoxy¹⁰; thus we believe that it should effectively cool the alkoxyes we have investigated this summer too. Despite this complication, a few conclusions can be drawn from the tentative origin assignments we have in Figure 15. As the size of the alkoxy has increased, the origin has generally shifted to the red. Furthermore, within a particular size, secondary isomers (in which the carbon bonded to the oxygen is bonded to two other carbons) have origins to the red of primary isomers.

Future Work

We have now obtained moderate-resolution spectra for virtually all of the alkoxy

species of significant spectroscopic interest. In the future, we will be performing *ab initio* calculations on these molecules to help with the vibronic analysis. The next step will be to obtain rotationally-resolved spectra of some of these larger alkoxies (which is done with a higher resolution dye laser). Rotationally resolved spectra are of interest because from them rotational constants can be found, which then yields geometric information about the molecule in both the ground and the excited state. This is quite useful information from the standpoint of reaction dynamics.

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