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 reactions\(^1-3\). The methoxy and ethoxy radicals\(^4,5\) (CH\(_3\)O and CH\(_3\)CH\(_2\)O, 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 alkoxy.

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 others\(^6-9\). 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 isomers\(^10\) (see Figure 1 for alkoxy structures). We were able to make a number of assignments of the different vibrational modes in these spectra using \textit{ab initio} calculations and also analogies between the larger and smaller alkoxy.

All of the alkoxy may be regarded as substituted versions of methoxy (CH\(_3\)O),
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 alkoxies 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 alkoxies 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 alkoxies
(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 \(\text{RONO}\)) via photolysis. The synthesis of the alkyl nitrites, which are not
commercially available, may be outlined as follows: \(\text{H}_2\text{SO}_4\) was added dropwise to a flask
containing \(\text{ROH}, \text{H}_2\text{O}, \text{and NaNO}_2\). \(\text{RONO}\) 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
\((\text{RONO} + h\nu \rightarrow \text{RO} + \text{NO})\) 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 $\text{s}$ delay between the
opening of the pulse valve and the photolysis laser trigger and another delay of about 10$\text{s}$
$s$ 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 $317-6 = 45$ 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 $ab$ \textit{initio}
calculations on some of the smaller alkoxyes). Some of these are: methyl torsions
($\approx 300$ cm$^{-1}$), backbone bends ($\approx 350$ cm$^{-1}$), C-C-O deformations ($\approx 400$ cm$^{-1}$), C-O
stretch (~550 cm\(^{-1}\)), and C-C stretches (~800 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 \textit{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 spectra\(^{10}\). This doesn’t seem to hold for larger alkoxies. 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 alkoxies 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 octoxies 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 alkoxies. 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 methoxy and 2-butoxy; thus we believe that it should effectively cool the alkoxies 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 \textit{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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\textbf{References}


