Jet-Cooled Laser Induced Fluorescence Spectroscopy of Some

Alkoxy Radicals

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Abstract

The laser induced fluorescence spectra of jet-cooled alkoxy radicals have been recorded. Spectra were observed for both isomers of propoxy and all three isomers of butoxy. In nearly all cases the vibrational structure of the spectra are dominated by a C–O stretch progression, which however terminates much more abruptly for the primary isomers than for the more branched ones. For each of the radicals (except t-butoxy) a number of low frequency (below the C–O stretch) vibrational modes have been assigned by analogies among the alkoxy spectra and reference to frequencies from ab initio calculations. A few higher frequency modes have also been assigned using similar approaches.
1 Introduction

Alkoxyl radicals (RO, where R=alkyl group) are expected intermediates in the oxidation of hydrocarbons, both in combustion environments and in our atmosphere. Indeed methoxy has been detected in flames and higher RO species are routinely included as intermediates in combustion codes. Given their chemical significance it is not surprising that their spectroscopic identification and characterization has long been pursued, with low resolution electronic spectra first being studied for methoxy, CH$_3$O, ethoxy, C$_2$H$_5$O, and 2-propoxy, HC(O)(CH$_3$)$_2$ years ago. The earlier work was mostly restricted to these three species, as well as the unsaturated vinoxy radical, C$_2$H$_3$O. However, driven by their likely significance in the oxidation of hydrocarbons, spectroscopic interest has been renewed and focussed upon larger RO species. The laser induced fluorescence (LIF) spectrum of two butoxy, C$_4$H$_9$O, isomers, 2-butoxy and t-butoxy, have recently been observed. Very recently we received a report of similar LIF experiments on two pentoxy radicals, 3-pentoxy, (CH$_3$CH$_2$)$_2$C(O)H and t-pentoxy, CH$_3$CH$_2$C(O)(CH$_3$)$_2$. In addition recent photodetachment experiments on their negative ions have yielded information on t-butoxy as well as several of the smaller alkoxy radicals.

The experiments involving the larger radicals are indeed exciting recent developments providing the first spectroscopic identification of, and information about, these species. However, all of them have been performed at or near room temperature with numerous vibrational hot bands present in the spectra as well as broad rotational contours. In earlier work we have reported the laser induced fluorescence (LIF) spectra of free jet cooled methoxy, ethoxy, and 2-propoxy radicals. For the first two species full rotational analyses have been carried out. In the case of methoxy, the rotational analyses led to definitive vibronic assignments based upon the rotational “bar coding” technique.

We believe that similar simplified free jet cooled spectra for the larger alkoxyl radicals will likewise prove very valuable. In most cases, it should be possible to rotationally analyze these spectra. Combining rotational bar coding and the elimination of most, if not all, the vibrational hot bands should lead ultimately to much more detailed vibronic assignments than are possible with only the hotter spectra.

This paper constitutes our first report of progress in what we expect will be a relatively detailed study of these cold free radicals. We report here the first observation of the jet-cooled spectra of the following
alkoxy radicals: 1-propoxy, 1-butoxy, 2-butoxy, and t-butoxy. We also include in our report, new spectra of the previously observed 2-propoxy radical, so that the present work includes all the isomers of the C$_3$H$_7$O and C$_4$H$_9$O radicals. In addition we have performed \textit{ab initio} calculations on all these species to help assign the vibrational structure in the spectra. Our present work is a prerequisite for rotationally resolved studies on these species, which we have just commenced.

2 Experimental

All the data was taken using a supersonic free-jet cooled expansion.\textsuperscript{26–28} The experimental setup consisted of a XeCl (Lambda Physik EMG103) pumped dye laser (Questek PDL3), with a linewidth of 0.1 cm$^{-1}$, which was used as the probe laser to take the LIF data for all the alkoxy. This work required the use of five laser dyes (PTP, DMQ, TMQ, BPBD, and Rhodamine 640). Photolysis of the precursor molecules was performed using a XeF (Lambda Physik ComPex110) excimer laser operating at 351 nm. The XeF radiation was employed after experiments using ArF (193 nm) and KrF (248 nm) radiation resulted in significantly reduced, or no detectable, alkoxy concentration. Approximately 75 mJ/pulse of the XeF photolysis beam was focussed 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 one inch 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.\textsuperscript{29} This was done for all the alkyl nitrites with the exception of 1-butylnitrite and t-butylnitrite which were commercially available from Acros (Fisher Scientific). The alkyl nitrite precursor was kept in a sample bomb at a temperature of about -5$^\circ$ C. A backing pressure of 100 psi helium was passed over the sample which was expanded into the chamber using a standard pulsed valve (General Valve) with a 500 $\mu$m orifice.

Even with jet expansion, spectra of some of the alkoxy radicals appeared to have a number of ‘hot’ bands in them, very similar to that seen in methoxy.\textsuperscript{22} For these species a teflon vibrational cooling fixture was placed on top of the nozzle. The teflon fixture was 5 mm in height with a hole for photolysis in the middle of the fixture. The channel through the fixture was 2mm in diameter. This type of fixture was shown\textsuperscript{23} to
be very effective in vibrationally cooling methoxy and performed similarly for the higher alkoxy radicals.

3 Results

All the alkoxy radicals can be viewed as substituted versions of methoxy, which with \( C_{3v} \) symmetry has a well known \( \tilde{A}^2A_1 - \tilde{X}^2E \) transition in the near UV that can be probed with LIF. For all the other alkoxy radicals (except \( t \)-butoxy - see below) the symmetry is lower and the \( \tilde{X}^2E \) state is resolved into a pair of states with the ground state designated \( \tilde{X} \) and the lowing-lying excited state designated \( \tilde{A} \). Thus the LIF experiments are carried out on the UV transition analogous to the one in methoxy, but now designated as \( \tilde{B} - \tilde{X} \) (except for \( t \)-butoxy).

The point group symmetry of the alkoxy radicals larger than methoxy is determined by the orientation of the methyl group(s). For our \textit{ab initio} calculations (see below) and for convenience in spectroscopic notation, we will assume the rotational position of the methyl groups is such that as to yield the highest point group symmetry. Thus we treat all the alkoxy radicals through the butoxy isomers as having \( C_s \) symmetry, except for \( t \)-butoxy and methoxy with \( C_{3v} \) symmetry and 2-butoxy with \( C_1 \) symmetry. Detailed studies\(^{25} \) of the rotational structure of ethoxy and 2-propoxy have shown that their ground states are \( \tilde{X}^2A’ \) and \( \tilde{X}^2A'' \) respectively, with a recent \textit{ab initio} calculation agreeing\(^{20} \) with these results, and correspondingly these symmetries were chosen for the ground state in our calculations. By analogy with ethoxy, 1-propoxy and 1-butoxy were also assumed to have \( 2A' \) ground states with, of course, 2-butoxy being simply \( 2A \). In the case of \( t \)-butoxy the question of the degeneracy of the \( \tilde{X}^2E \) ground state and possible Jahn-Teller effects therein remains an open one. The \( \tilde{B} \) excited state of the alkoxy is taken to be \( 2A' \) symmetry, except for \( 2A \) symmetry in 2-butoxy, with of course the corresponding state for the \( C_{3v} \) species being \( \tilde{A}^2A_1 \).

In this section we discuss the vibrational structure of the various \( \tilde{B} - \tilde{X} \) alkoxy LIF spectra, emphasizing the similarities in overall structure, and where appropriate also indicating the differences. Our assignments of vibrational lines rest principally upon analogies that originate in the spectrum of ethoxy and can be extrapolated to the propoxy and butoxy isomers. We have also run \textit{ab initio} calculations with Gaussian98 on all the alkoxy radicals. These were CIS calculations with a 6-31+G* basis set. Unfortunately due to the difficulties of calculating excited states, especially for low symmetry molecules, the vibrational frequencies are not
quantitatively accurate compared with experiment. Nonetheless, they are extremely useful for ordering the frequencies (see below) and getting an understanding of the geometric nature of the modes.

As with methoxy\textsuperscript{21} and ethoxy,\textsuperscript{11,24} all the observed spectra (except possibly 1-butoxy – see below) are dominated by a progression in the C–O stretch mode, as the bond length increases significantly in going from the $\tilde{X}$ to the $\tilde{B}$ state. It is therefore convenient to divide the observed vibrations into a low frequency set (below the C–O stretch) and a high frequency set (above the C–O stretch). Based upon an analysis\textsuperscript{11} of the $\tilde{B}^2A' - \tilde{X}^2A'$ LIF spectrum, this classification seems to work well for the $\tilde{B}^2A'$ state of ethoxy. For it there are two low frequency modes, the methyl torsion (244 cm\textsuperscript{$-1$}) and the CCO deformation (362 cm\textsuperscript{$-1$}). The observed high frequency set consists of the C–C stretch (869 cm\textsuperscript{$-1$}) and a CH\textsubscript{2} rocking (893 cm\textsuperscript{$-1$}). A couple of other, mainly H atom, modes have been identified well above 1000 cm\textsuperscript{$-1$} for ethoxy, but the corresponding motions are difficult to pick out of the relatively dense spectra of the larger alkoxies. It should be pointed out that in the C\textsubscript{s} symmetry assumed for ethoxy, neither the torsion nor the CH\textsubscript{2} rock are totally symmetric and hence they are electronically forbidden. However they are vibronically allowed, and appear, albeit rather weakly, in the excitation spectrum. For the larger species, such symmetry restrictions may have even less significance. Below we offer what we believe are the most likely assignments for a number of the observed vibrational bands. As with any assignments of this nature, they cannot be considered totally conclusive, but we believe that they are consistent with all the presently available information. Placement of these assignments on firmer ground will require additional information as may be forthcoming, for example, from the rotational analyses.

3.1 Propoxy Isomers

There are two isomers for propoxy. The linear chain isomer, 1-propoxy, is most analagous to ethoxy. The branched chain isomer we denote as 2-propoxy although it is often referred to as isoproxy.

3.1.1 2-propoxy

The 2-propoxy spectrum is shown in Fig. 1. As expected there is a strong progression of the C–O stretch with levels up to v=7 marked in the figure. We have analyzed this progression with the usual power series
expression in \((v+1/2)\) and give values in Table 1 for \(\omega_c\) and \(\omega_c x_c\) as well as \(T_{00}\), the origin frequency. We believe that the weakness of the last few observed members \((v=5-7)\) of the progression arises from reduced quantum yield due to non-radiative processes.

The low frequency region of the spectrum is expanded in Fig. 2 and shows 5 distinct transitions. Given the cleanness of the region in the immediate vicinity of the origin it is unlikely that any of these are hot bands. Correspondingly none of these lines have frequencies consistent with their being combinations or overtones. It is therefore likely that each band terminates on a fundamental in the \(\tilde{B}\) state. Our \textit{ab initio} calculations indicate there are 5 such fundamentals in the low frequency region. We believe that the most likely assignments of the low frequency observed frequencies, labelled 1-5 in Fig. 2, are as follows. The two lowest frequency transitions (numbers 1 and 2) are assigned to an out-of-phase methyl torsion (344 cm\(^{-1}\)) and an in-phase one (357 cm\(^{-1}\)). The weak line (number 3) between the two doublets is likely a C–C–C backbone bend (378 cm\(^{-1}\)) and the high frequency pair (numbers 4 and 5) we assign respectively to an asymmetric C–C–O deformation (449 cm\(^{-1}\)) and a symmetric one (466 cm\(^{-1}\)). Clearly the assignments for the members of the pairs could easily be interchanged. Our present assignments are guided by the order of the frequencies from the \textit{ab initio} calculations.

Above the C–O stretch there is a repetition of the low frequency structure in a series of combination bands. As one goes to higher frequencies, there also appear to be several additional lines (labelled a-d in Fig. 2) that likely correspond to fundamentals at 860, 938, 1152, 1212 cm\(^{-1}\). However with the quality of the calculations, it is difficult to suggest assignments for most of these lines. Nonetheless the strongest and lowest frequency one (a) may well correspond to primarily the C–C stretch.

### 3.1.2 1-propoxy

We apply much the same logic to the 1-propoxy spectrum as we did for that of 2-propoxy. As Fig. 3 shows, the strongest band in the spectrum, at 582 cm\(^{-1}\) above the origin, is assigned as the C–O stretch. It is the only member of the C–O stretch progression observed in 1-propoxy indicating a non-radiative channel sets in at low excitation energies above the vibrationless level of the \(\tilde{B}\) state. In analogy with work\(^{30-32}\) on CH\(_3\)O we suspect that this channel is photofragmentation into O plus a propyl radical. Clearly this process occurs
at lower energy, referenced to $T_{00}$, in the primary propoxy radical compared to the secondary one.

The low frequency region of the spectrum again contains several weak transitions that nonetheless can be seen rather clearly in Fig. 3. The *ab initio* calculations suggest four fundamentals in this region and we assign the four observed lines, labelled 1-4 in Fig. 3, to these fundamentals. In 1-propoxy there is expected a low frequency backbone flex which we ascribe to the line (1) observed at 149 cm$^{-1}$. The methyl torsion is assigned to the 203 cm$^{-1}$ line (2) and the 260 cm$^{-1}$ line (3) likely corresponds to the C–C–C bend. Finally the 311 cm$^{-1}$ line (4) is assigned to the C–C–O deformation. Again we have followed the order of the frequencies of the *ab initio* calculation to make these assignments.

Above the C–O stretch several weak lines (labelled a-d in Fig. 3 and at respectively 647, 785, 796, 969 cm$^{-1}$) are observed that are likely also fundamentals. The *ab initio* calculations suggest a number of fundamentals lie in this region, but given their quality (and the often mixed character of the motion), it does not seem fruitful to attempt individual assignments. However, there is one strong transition at 818 cm$^{-1}$ which is almost certainly analogous to the 860 cm$^{-1}$ band in 2-propoxy. Again we suggest that this band carries significant C–C stretch character.

### 3.2 Butoxy Isomers

We obviously attempt to extend the vibrational assignments of the smaller ethoxy and propoxy species to the butoxy radicals. Clearly the larger the radical the less precise the assignment and description of the vibration; however, for butoxy it appears that a number of useful characterizations can still be made.

In Figs. 4, 5 and 6 we show respectively the LIF excitation spectra of 2-butoxy, t-butoxy, and 1-butoxy. Both the branched chain isomers appear to show more hot band structure than the primary butoxy radical. It appears that the recoil of NO leaving from a branched chain point allows more energy to be stored in the internal vibrations of the resulting alkoxy radical. This excess vibrational energy is incompletely cooled in the jet expansion thereby producing the hot bands. These hot bands can largely be eliminated by use of an extension on the nozzle as described in the experimental section. However the extension also reduces the signal/noise somewhat even for cold bands, so that it is impossible to be certain whether some of the weaker bands in the spectra of the branched chain isomers are truly hot or cold.
3.3 2-butoxy

In Fig. 4 we again see a spectrum dominated by one excitation of the C–O stretch. Its C–O stretch frequency along with $T_{00}$ is given in Table 1. Comparing the two traces of Fig. 4 the only transitions besides the C–O stretch that can be judged with certainty to be cold bands are labelled 1, a, and b. Based upon the calculated values of the low frequency bands, it appears that the band labelled 1 (470 cm$^{-1}$) in Fig. 4 likely corresponds to one of the two C–C–O deformation modes. When we look at the calculated frequencies above the C–O stretch we note a large number of modes with quite mixed motions involving CH$_2$ wagging, methyl rocking and C–C stretch. There are, however, two modes with strong contributions from the C–C stretch and we somewhat arbitrarily, but analogously to the propoxy spectra, assign the observed a (729 cm$^{-1}$) and b (918 cm$^{-1}$) bands to these fundamentals.

3.4 t-butoxy

As Fig. 5 shows the spectrum of t-butoxy is probably the most complex observed and it also is relatively weak. What is immediately obvious from Fig. 5 is that we have recovered a relatively long progression (at least 7 members) in the C–O stretch. Clearly this most branched butoxy isomer is less susceptible to photofragmentation than the primary or secondary butoxies. The t-butoxy C–O stretch frequency as well as its $T_{00}$ value is listed in Table 1.

The signal/noise of the spectrum makes assigning any of the weak, low-frequency transitions essentially impossible. The only relatively strong low frequency band observed is at 311 cm$^{-1}$ above the origin, labelled 1 in Fig. 5, which puts it in the range expected for methyl torsion; it is also observed at higher frequencies in combination with the C–O stretch. Above the C–O stretch there appears to be several additional fundamentals. Three of these bands have been labelled a, b, and c, at respectively 760, 855, and 975 cm$^{-1}$; these likely contain significant C–C stretch along with some CH$_2$ wag and methyl rock motion. These bands are also observed at higher frequencies in combination with the C–O stretch.
3.5 1-butoxy

Fig. 6 shows the spectrum of 1-butoxy. At first glance the spectrum appears very much like those of the other alkoxies with a dominant progression involving the C–O stretch. However, if we assign the strongest line in the spectrum to the C–O stretch we get an anomalously low frequency of 444 cm$^{-1}$ rather than a frequency of around 560-580 cm$^{-1}$, expected from the other C–O stretching values in Table 1. Indeed there are 4 relatively strong lines in this vicinity of the spectrum (444, 512, 612, and 710 cm$^{-1}$ and labelled in Fig. 6 a-d respectively). A simple average of these lines leads to a frequency of 570 cm$^{-1}$, close to the expected C–O stretch value. The \textit{ab initio} calculation suggests at least a couple of fundamentals in this region. Therefore we expect that there may well be a Fermi resonance occurring that distributes the C–O stretch band intensity over several lines.

The low frequency portion of the spectrum is somewhat easier to interpret. The calculations suggest that six fundamentals lie below 400 cm$^{-1}$ in decreasing frequency: a C–C–O deformation, a C–C–C–C bend, methyl torsion, another C–C–C–C bend, and finally a pair of backbone flexing modes. Based qualitatively on the calculated frequencies, as well as the assignments in 1-propoxy and ethoxy we suggest the following assignments for the four observed bands labelled 1-4 of 1-butoxy. The pair (3 and 4) at 324 and 334 cm$^{-1}$ correspond to a C–C–C–C bend and the C–C–O deformation. The 271 cm$^{-1}$ mode (2) may be the other C–C–C–C bend while the 207 cm$^{-1}$ band (1) is likely the methyl torsion. This assignment would imply that we do not observe either of the backbone flexes. However the flex was a quite weak band in 1-propoxy and one would expect the corresponding bands to be at even lower frequencies in butoxy (compared to propoxy) where no bands are observed experimentally.

4 Discussion

Of the alkoxy radicals discussed in this paper, only the 2-propoxy radical has been previously observed under jet-cooled conditions. However the report\textsuperscript{25} on 2-propoxy only considered the rotational structure of the $0^0_0$ band and no vibrational analysis was performed. Near ambient, i.e., $\lesssim 200$K, spectra have been reported for the other radicals, except 1-propoxy and 1-butoxy, and in each case the dominant C-O stretch
vibration has been identified and our present results, except for some increased precision, are consistent with the previously reported C–O stretch frequencies.\textsuperscript{15,17–19} As far as we are able to ascertain the additional vibrational frequencies reported in this paper for these radicals have not been reported previously.

There are, however, additional results\textsuperscript{14,15,17,18} that should be considered. Finke, et al.\textsuperscript{14} report no spectroscopic information about the \textit{t}-butoxy radical that they reported observing via LIF. They do however claim that in the photodissociation of \textit{t}-butyl nitrite, \textit{t}-butoxy is produced in the \textit{\tilde{B}} state. We observed relatively strong background fluorescence in our LIF experiments on \textit{t}-butoxy which may be consistent with radiative decay of excited \textit{\tilde{B}} state butoxy. Dibble \textit{et al.},\textsuperscript{15} Lotz and Zellner,\textsuperscript{17} and Blitz \textit{et al.}\textsuperscript{18} have reported some spectroscopic information from experiments being done at or near room temperature, with the most detailed spectroscopic study being that done by Dibble and co-workers. Our C–O stretch frequency and origin frequency are consistent with those previously reported. However, Dibble \textit{et al.}\textsuperscript{15} report a second strong vibrational progression with a frequency decreasing from 546–495 cm\textsuperscript{{-1}}. We see no corresponding series in our jet-cooled \textit{t}-butoxy spectrum, so we suspect that this progression is built on a vibrational hot band.

Again for 2-butoxy, the reported\textsuperscript{15} \textit{T}_\text{00} (26185 cm\textsuperscript{−1}) is far to the red of the apparent origin (26757 cm\textsuperscript{−1}) in our jet-cooled spectrum. We have made an extensive search for additional peaks to the red of 26757 cm\textsuperscript{−1}, without success. While there is always the possibility that the intensity of lower members of the progression are below our detection limit, comparison of the present Fig. 4 with Fig. 3 of ref. 15 makes that possibility fairly unlikely. Indeed, the authors of ref. 15 have recently suggested the origin of 2-butoxy ought to reassigned to 26774 cm\textsuperscript{−1} based upon the trend among origin frequencies of the various alkoxies.\textsuperscript{19} In addition we find no analogue in our spectrum of the 556, 602, and 624 cm\textsuperscript{−1} progressions identified in their report.

When one compares Fig. 3 of ref. 15 and our LIF spectrum of 2-butoxy, one is struck by the fact that the C–O progression apparently extends to higher frequency. Table 2 in ref. 15 lists frequencies for the C–O stretch progression up to 3–0 while we were only able to observe one quantum of the C–O stretch in our jet-cooled spectrum. One way that the two spectra can be reconciled is to assume that under the conditions of the warmer spectrum, vibrational relaxation effectively competes with photofragmentation in the \textit{v}=2 and
3 C–O stretch levels, giving rise to \( v=1 \) (or 0) fluorescence from molecules originally excited to the higher levels. Such vibrational relaxation is unlikely present in the cold jet experiment.

There have been no previous reports of a LIF spectrum for 1-butoxy. Wang et al.\(^{19}\) reported only being able to observe a diffuse spectrum or formaldehyde lines while searching for the 1-butoxy radical.\(^ {19}\) Hein and co-workers reported on reactions of 1-butoxy but did not directly detect the alkoxy.\(^ {33}\) As we mentioned earlier the spectrum we attribute to 1-butoxy is different from all the other known alkoxy spectra in that there is no strong band or progression, easily ascribable to the C–O stretch. The explanation of Fermi resonance, to account for the absence of a band clearly assignable to the C–O stretch seems fairly reasonable. Nonetheless the observations of Wang, et al. led to some doubt about assigning this spectrum to 1-butoxy. To help confirm our assignment we took a higher resolution scan of the band labelled a to reveal partially resolved rotational structure. As Fig. 7 shows the match between the observed structure and that expected for 1-butoxy from \textit{ab initio} calculations is quite reasonable. While higher resolution results are desirable (and experiments are in progress to obtain them), the presently observed rotational structure adds considerable credence to our assignment of the carrier of this spectrum to 1-butoxy.

5 Conclusions

By cooling the propoxy and butoxy radicals in a supersonic free jet expansion, much simpler and more assignable LIF spectra have been obtained than previously reported. From a spectroscopic point of view these spectra yield excellent values for \( T_{00} \), the C–O stretch and numerous low frequency vibrations. Comparison of the present cold spectra with those taken at ambient or nearer ambient temperatures indicate that the latter likely contain many hot bands leading to ambiguous assignments.

From a dynamical point of view, we find marked differences between the primary and branched alkoxy isomers. Photolysis of the alkyl nitrite leads to much hotter nascent distributions for the more branched isomers. In the excited state, non-radiative processes appear to dominate the decay at much lower energies (relative to the vibrationless level) for the primary, compared to the branched, radicals.
6 Acknowledgments

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References

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and Flame 1999, 118, 415.


Figure Captions

1. Survey scan of the LIF excitation spectrum of jet-cooled 2-propoxy. The members of the C–O stretch progression are indicated. Although barely visible on this scan the observability of the \( v=7 \) member of the progression was confirmed on other narrower scans.

2. Expanded view of the low frequency region of the jet-cooled LIF excitation spectrum of 2-propoxy. Fundamentals below the \( v=1 \) of the C–O stretch are numbered 1-5, while others identified above the C–O stretch frequency are labelled a-d. See text for details of the assignments.

3. LIF excitation spectrum of jet-cooled 1-propoxy. The fundamentals of the C–O and C–C stretch are marked respectively \( \nu_{C-O} \) and \( \nu_{C-C} \). Fundamentals below the \( v=1 \) of the C–O stretch are numbered 1-4, while others identified above the C–O stretch frequency are labelled a-d. See text for details of the assignment. The line labelled \( \nu_{C-O} \) extends off-scale so as to show more clearly the weaker transitions.

4. LIF excitation of jet-cooled 2-butoxy: B) with a cooling extension to reduce vibrational hot bands and A) without it. The intensity of the C–O stretch band in A) is somewhat saturated. In addition to the C–O stretch fundamental, indicated \( \nu_{C-O} \), three other transitions could be identified as cold fundamentals and are labelled 1, a, and b in increasing frequency. See text for the assignments of these bands.

5. LIF excitation spectrum of jet-cooled t-butoxy. The long C–O stretch progression is indicated.

6. LIF excitation spectrum of jet-cooled 1-butoxy. Low frequency fundamentals are labelled 1-4. A series of relatively strong bands in the vicinity of the expected C–O stretch fundamental are labelled a-d. See text for the details of these assignments.

7. Higher resolution scan (A) of the LIF excitation spectrum of band a in Fig. 6. In (B) is shown a simulated plot of the rotational structure expected for 1-butoxy using the rotational constants obtained from our \textit{ab initio} calculations.
Table 1: Origin and C-O stretch frequencies (cm$^{-1}$) for various alkoxy radicals.

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$^a$ From Foster et al. ref.[25] and Powers, et al. ref.[23]

$^b$ From Tan et al. ref.[24].

$^c$ From Zhu et al. ref.[11].

$^d$ Frequency for the $v_{C-O} = 0 - 1$ separation.

$^e$ For comments on the C-O stretch frequency, see text.
Figure 1: Survey scan of the LIF excitation spectrum of jet-cooled 2-propoxy. The members of the C–O stretch progression are indicated. Although barely visible on this scan the observability of the $v=7$ member of the progression was confirmed on other narrower scans.
Figure 2: Expanded view of the low frequency region of the jet-cooled LIF excitation spectrum of 2-propoxy. Fundamentals below the $\nu=1$ of the C–O stretch are numbered 1-5, while others identified above the C–O stretch frequency are labelled a-d. See text for details of the assignments.
Figure 3: LIF excitation spectrum of jet-cooled 1-propoxy. The fundamentals of the C–O and C–C stretch are marked respectively $\nu_{C-O}$ and $\nu_{C-C}$. Fundamentals below the $v=1$ of the C–O stretch are numbered 1-4, while others identified above the C–O stretch frequency are labelled a-d. See text for details of the assignment. The line labelled $\nu_{C-O}$ extends off-scale so as to show more clearly the weaker transitions.
Figure 4: LIF excitation of jet-cooled 2-butoxy: B) with a cooling extension to reduce vibrational hot bands and A) without it. The intensity of the C–O stretch band in A) is somewhat saturated. In addition to the C–O stretch fundamental, indicated $\nu_{C-O}$, three other transitions could be identified as cold fundamentals and are labelled 1, a, and b in increasing frequency. See text for the assignments of these bands.
Figure 5: LIF excitation spectrum of jet-cooled t-butoxy. The long C–O stretch progression is indicated.
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Figure 7: Higher resolution scan (A) of the LIF excitation spectrum of band a in Fig. 6. In (B) is shown a simulated plot of the rotational structure expected for 1-butoxy using the rotational constants obtained from our \textit{ab initio} calculations.