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# Jet-Cooled Laser-Induced Fluorescence Spectroscopy of Some Alkoxy Radicals

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The laser-induced fluorescence spectra of jet-cooled alkoxy radicals were 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 were assigned by analogies among the alkoxy spectra and reference to frequencies from ab initio calculations. A few higher frequency modes were also assigned using similar approaches.

## 1. Introduction

Alkoxy 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,[1] and higher RO species are routinely included as intermediates in combustion codes.[2−4] 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[5−11] for methoxy, $CH_3O$; ethoxy, $C_2H_5O$; 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,[12,13] $C_2H_3O$. However, driven by the likely significance of these compounds in the oxidation of hydrocarbons, spectroscopic interest has been renewed and focused on larger RO species. The laser-induced fluorescence (LIF) spectrum of two butoxy ($C_4H_9O$) isomers, 2-butoxy and *t*-butoxy, have recently been observed.[14−18] Very recently, we received a report of similar LIF experiments on two pentoxy radicals, 3-pentoxy ($(CH_3CH_2)_2C(O)H$) and *t*-pentoxy ($CH_3CH_2C(O)(CH_3)_2$). In addition, recent photodetachment experiments[20] 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, with 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 ($\gtrsim$200 K), 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,[21−23] ethoxy,[24] and 2-propoxy radicals.[25] For the first two species, full rotational analyses were 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 alkoxy 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 $C_3H_7O$ and $C_4H_9O$ radicals. In addition, we performed 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 Section

All data were taken using a supersonic free jet-cooled expansion.[26−28] 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 the alkoxys. 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 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.[29] This was done for all the alkyl nitrites with the exception of 1-butylnitrite and *tert*-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 °C. A backing pressure of 100 psi

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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.[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 2 mm in diameter. This type of fixture has been shown[23] to be very effective in vibrationally cooling methoxy, and it 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 (expect *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 lowest 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 alkoxies larger than methoxy is determined by the orientation of the methyl group(s). For our ab initio calculations (see below) and for convenience in spectroscopic notation, we will assume that the rotational position of the methyl groups is that which will 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 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 alkoxies is taken to be of $^2A'$ 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 on analogies that originate in the spectrum of ethoxy and can be extrapolated to the propoxy and butoxy isomers. We have also run ab initio calculations with Gaussian98 on all the alkoxies. 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[21] and ethoxy,[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 on an analysis[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 this spectrum there are two low-frequency modes, the methyl torsion (244 cm$^{-1}$) and the CCO deformation (362 cm$^{-1}$). The observed high-frequency set consists of the C−C stretch (869 cm$^{-1}$) and a $CH_2$ rock (893 cm$^{-1}$). A couple of other, mainly H-atom, modes were identified well above 1000 cm$^{-1}$ 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 $C_s$ symmetry assumed for ethoxy, neither the torsion nor the $CH_2$ 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.

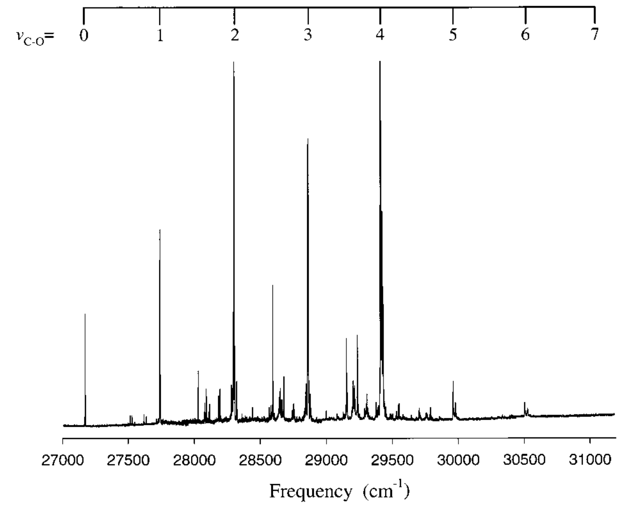

**Figure 1.** Survey scan of the LIF excitation spectrum of jet-cooled 2-propoxy. The members of the C−O stretch progression are indicated. Although barely visible on this scan, the observability of the $\nu = 7$ member of the progression was confirmed on other narrower scans.

**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 Figure 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 ($\nu$ + 1/2) and give values in Table 1 for $\omega_e$ and $\omega_e x_e$ as well as $T_{00}$, the origin frequency. We believe that the weakness of the last few observed members ($\nu = 5-7$) of the progression arises from reduced quantum yields due to nonradiative processes.

The low-frequency region of the spectrum is expanded in Figure 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 ab initio calculations indicate that there are 5 such fundamentals in the low-frequency region. We believe that the most likely assignments of the low-

**TABLE 1: Origin and C−O Stretch Frequencies ($cm^{-1}$) for Various Alkoxy Radicals**

| species | origin | $\omega_e$ | $\omega_e x_e$ |
|---|---|---|---|
| methoxy[a] | 31614 | 677.2 | 4.6 |
| ethoxy | 29210[b] | 609[c] | 3.0[c] |
| 2-propoxy | 27171 | 574.4 | 5.2 |
| 1-propoxy | 28634 | 582[d] | − |
| 2-butoxy | 26757 | 559[d] | − |
| *t*-butoxy | 25861 | 546 | 3.1 |
| 1-butoxy[e] | 28649 | − | − |

[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 $\nu_{C-O} = 0 - 1$ separation. [e] For comments on the C−O stretch frequency, see text.

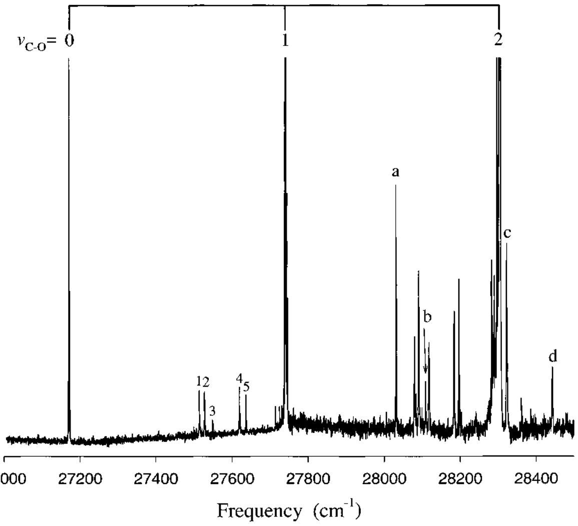

**Figure 2.** Expanded view of the low-frequency region of the jet-cooled LIF excitation spectrum of 2-propoxy. Fundamentals below the $\nu = 1$ of the C−O stretch are numbered 1−5, whereas others identified above the C−O stretch frequency are labeled a−d. See text for details of the assignments.

frequency observed transitions, labeled 1−5 in Figure 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 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 (labeled a−d in Figure 2) that likely correspond to fundamentals at 860, 938, 1152, and 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 Figure 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 that a nonradiative channel sets in at low excitation energies above the vibrationless level of the $\tilde{B}$ state. In analogy with work[30−32] on $CH_3O$, 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.

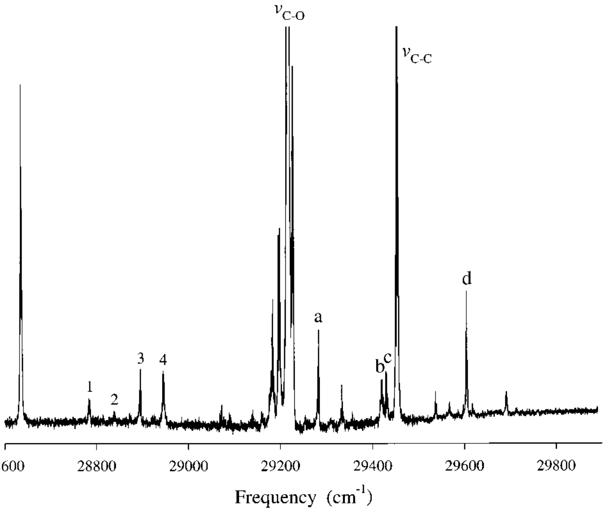

**Figure 3.** LIF excitation spectrum of jet-cooled 1-propoxy. The fundamentals of the C−O and C−C stretches are marked respectively $\nu_{C-O}$ and $\nu_{C-C}$. Fundamentals below the $\nu = 1$ of the C−O stretch are numbered 1−4, whereas others identified above the C−O stretch frequency are labeled a−d. See text for details of the assignment. The line labeled $\nu_{C-O}$ extends off-scale so as to show more clearly the weaker transitions.

The low-frequency region of the spectrum again contains several weak transitions that nonetheless can be seen rather clearly in Figure 3. The ab initio calculations suggest four fundamentals in this region, and we assign the four observed lines, labeled 1−4 in Figure 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 (labeled a−d in Figure 3 and at respectively 647, 785, 796, and 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 $cm^{-1}$ that 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 attempted 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 Figures 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.

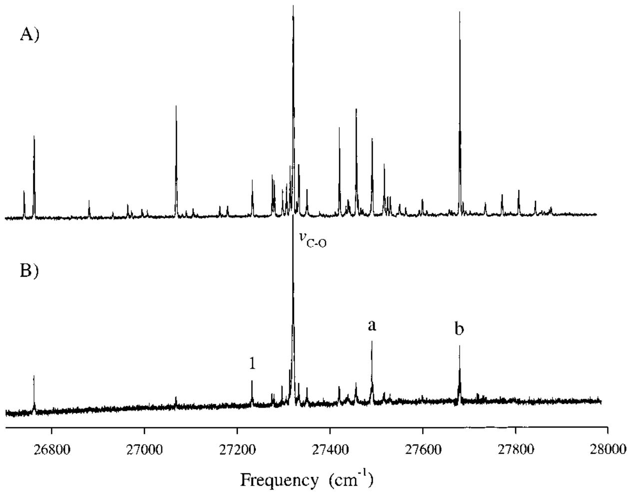

**Figure 4.** LIF excitation of jet-cooled 2-butoxy: (B) with a cooling extension to reduce vibrational hot bands and (A) without it. The intensity of the C−O stretch band in (A) is somewhat saturated. In addition to the C−O stretch fundamental, indicated $\nu_{C-O}$, three other transitions could be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

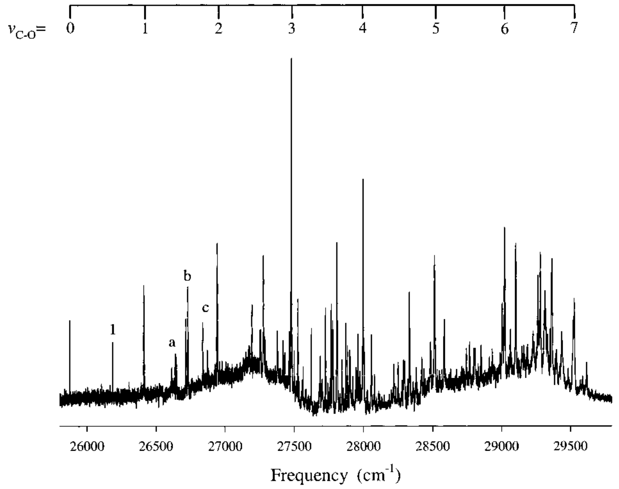

**Figure 5.** LIF excitation spectrum of jet-cooled *t*-butoxy. The long C−O stretch progression is indicated.

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 ratio 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 Figure 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 Figure 4, the only transitions besides the C−O stretch that can be judged with certainty to be cold bands are labeled 1, a, and b. On the basis of the calculated values of the low frequency bands, it appears that the band labeled 1 (470 cm$^{-1}$) in Figure 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 stretching. 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.

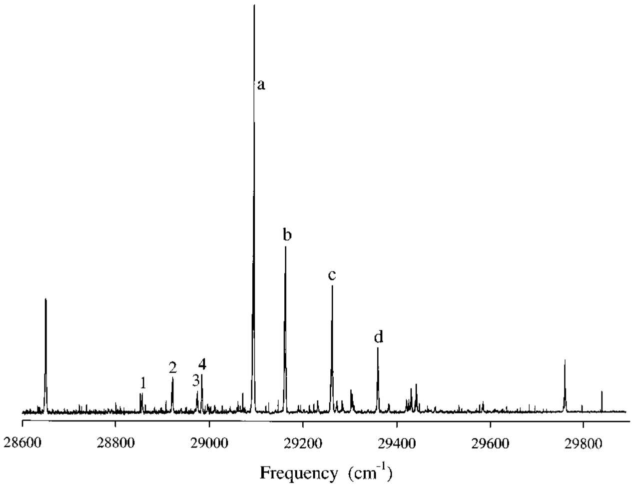

**Figure 6.** LIF excitation spectrum of jet-cooled 1-butoxy. Low-frequency fundamentals are labeled 1−4. A series of relatively strong bands in the vicinity of the expected C−O stretch fundamental are labeled a−d. See text for the details of these assignments.

**3.4. *t*-Butoxy.** As Figure 5 shows, the spectrum of *t*-butoxy is probably the most complex observed, and it also is relatively weak. What is immediately obvious from Figure 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 ratio 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, labeled 1 in Figure 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 are labeled a, b, and c, at, respectively, 760, 855, and 975 cm$^{-1}$; these likely contain significant C−C stretching along with some $CH_2$ waging and methyl rocking motions. These bands are also observed at higher frequencies in combination with the C−O stretch.

**3.5. 1-Butoxy.** Figure 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$^{-1}$ that is 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 labeled in Figure 6a−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 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 labeled 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, whereas 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[25] on 2-propoxy only considered the rotational structure of the $0_0^0$ band and no vibrational analysis was performed. Near ambient, that is, $\gtrsim 200$ 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; our present results, except for some increased precision, are consistent with the previously reported C−O stretch frequencies.[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[14,15,17,18] that should be considered. Finke et al.[14] report no spectroscopic information about the *t*-butoxy radical that they reported observing via LIF. They do, however, claim that in the photodissociation of *t*-butyl nitrite, *t*-butoxy is produced in the $\tilde{B}$ state. We observed relatively strong background fluorescence in our LIF experiments on *t*-butoxy, which may be consistent with radiative decay of excited $\tilde{B}$ state butoxy. Dibble et al.,[15] Lotz and Zellner,[17] and Blitz et al.[18] have reported some spectroscopic information from experiments 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 et al.[15] report a second strong vibrational progression with a frequency decreasing from 546 to 495 cm$^{-1}$. We see no corresponding series in our jet-cooled *t*-butoxy spectrum, so we suspect that this progression is built on a vibrational hot band.

For 2-butoxy, the reported[15] $T_{00}$ (26 185 cm$^{-1}$) is far to the red of the apparent origin (26 757 cm$^{-1}$) in our jet-cooled spectrum. We have made an extensive search for additional peaks to the red of 26 757 cm$^{-1}$, without success. Although there is always the possibility that the intensity of lower members of the progression are below our detection limit, comparison of the present Figure 4 with Figure 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 be reassigned to 26 774 cm$^{-1}$ based on the trend among origin frequencies of the various alkoxies.[19] In addition, we find no analogue in our spectrum of the 556, 602, and 624 cm$^{-1}$ progressions identified in their report.

When one compares Figure 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, whereas 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 $\nu = 2$ and 3 C−O stretch levels, giving rise to $\nu = 1$ (or 0) fluorescence from molecules originally excited to the higher levels. Such vibrational relaxation is unlikely to be present in the cold jet experiment.

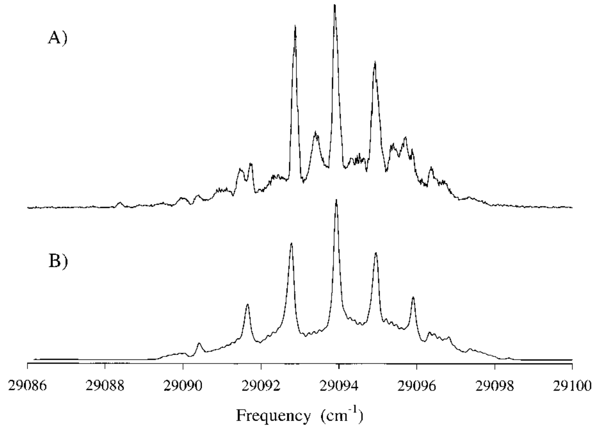

**Figure 7.** Higher resolution scan (A) of the LIF excitation spectrum of band a in Figure 6. In (B) is shown a simulated plot of the rotational structure expected for 1-butoxy using the rotational constants obtained from our ab initio calculations.

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 labeled a to reveal partially resolved rotational structure. As Figure 7 shows, the match between the observed structure and that expected for 1-butoxy from ab initio calculations is quite reasonable. Although 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 near 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, nonradiative processes appear to dominate the decay at much lower energies (relative to the vibrationless level) for the primary, compared to the branched, radicals.

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