The rotationally resolved electronic spectra of several conformers of 1-hexoxy and 1-heptoxy¹

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Abstract: Laser-induced fluorescence excitation spectra of five vibronic bands of 1-hexoxy and three bands of 1-heptoxy have been recorded in a jet-cooled environment. Experimental values of rotational constants for both the \tilde{X} and \tilde{B} states and components of the spin-rotational tensor for the \tilde{X} state were obtained by an analysis of the partially resolved rotational structure of the vibronic bands. Comparing these experimental results with quantum chemistry calculations, and using corresponding assignments of smaller alkoxy radicals as a guide, permitted unambiguous conformational assignments for the bands. The extension of similar assignments to larger alkoxy radicals is also discussed.

Key words: electronic spectroscopy, organic radicals, combustion, atmospheric chemistry.

Résumé: Les spectres de fluorescence induite par laser de cinq bandes vibroniques du 1-hexoxy et de trois bandes du 1-heptoxy ont été enregistrés en jet froid. Une analyse de la structure rotationnelle partiellement résolue des bandes vibroniques a permis d'obtenir les valeurs expérimentales des constantes rotationnelles des deux états \tilde{X} et \tilde{B} , ainsi que les composantes tensorielles de spin-rotation de l'état \tilde{X} . La comparaison des résultats expérimentaux avec des calculs de chimie quantique, ainsi qu'une utilisation des attributions correspondantes de plus petits radicaux alkoxy comme guide, a permis une attribution des conformères sans ambiguité possible pour chaque bande. L'extension d'attribution similaire à de plus gros radicaux de type alkoxy est discutée.

Mots clés: spectroscopie électronique, radicaux organiques, combustion, chimie de l'atmosphère.

[Traduit par la Rédaction]

1. Introduction

It is a privilege to contribute to this Gerhard Herzberg memorial issue. One of his abiding interests was the spectroscopy of free radicals (1). Arguably his electronic spectra of the simplest hydrocarbon free radicals (2–6) CH, CH₂, and CH₃, rank among the most significant achievements in his illustrious career.

In this spirit, this paper reports the electronic spectroscopy of some simple hydrocarbon-derived, oxygen-containing, free radicals, the alkoxies ($C_nH_{2n+1}O$). The importance of alkoxy radicals in atmospheric chemistry is well known (7). They are key intermediates in the oxidation of hydrocarbons. More than 100 studies have been published alone over the last 50 years on the spectroscopic studies of the smallest alkoxy radical, methoxy. Other small alkoxies like ethoxy (8,9), C_2H_5O , and 2-propoxy (9, 10), (CH₃)₂HCO, have also been studied intensively.

The early laser magnetic resonance investigation of Radford and Russell (11) in the far-IR and the microwave studies of Endo et al. (12) yielded considerable information about the ground ²E state of methoxy. Its electronic transition has long been known to be an excitation from the ground \tilde{X}^2 E state to the \tilde{A}^2 A state (13). When a hydrogen is substituted in methoxy, the C_{3v} symmetry of CH₃O is at least lowered to C_s; the excited \tilde{A} A₁ state of CH₃O correlates to a \tilde{B} A' state while the degenerate E ground state decomposes into \widetilde{A} and \widetilde{X} states, of A' and A'' symmetry assuming a plane of symmetry exists. Whether the \widetilde{X} state is A' or A'' depends upon the radical. Tan et al. (14) determined the symmetry of the \widetilde{X} and \widetilde{A} electronic states of ethoxy, vinoxy, and isopropoxy, using the technique of laser-induced fluorescence (LIF) combined with supersonic jet cooling. The complete rotational analysis of the LIF spectrum of the ethoxy (14) $\widetilde{B} - \widetilde{X}$ transition further revealed a significant ground-state, spin-rotation splitting due to the close spacing of the low-lying \widetilde{A} and \widetilde{X} states. Within experimental resolution ($\approx 200 \text{ MHz}$) no excited-state, spin-rotation splitting was observed.

While the smaller alkoxy radicals have drawn significant attention, the spectroscopic study of larger alkoxy radicals is much sparser. It was generally felt that the fluorescence quantum yield for the $\tilde{B} - \tilde{X}$ transition would rapidly decrease as non-radiative decay processes became dominant in the larger alkoxy radicals. That perception began to change when LIF spectra of *t*-pentoxy, 3-pentoxy, *t*-butoxy, and 2-butoxy were observed at near ambient temperature in 1999 (15, 16). However, the failed attempts to observe several other larger alkoxy radicals in the same LIF studies left the overall situation unclear. Clarification occurred when the LIF spectra of nearly 20 large alkoxy radicals containing 5–12 carbon atoms were reported by Carter et al. (17) in 2001. The studies showed that under

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Fig. 1. Structures of representative examples of the (a) 41 1-hexoxy conformers and (b) 122 1-heptoxy conformers. The corresponding Newman projections are also shown.



cold jet conditions, all of the alkoxy radicals exhibit sharp LIF excitation spectra with well-characterized vibrational structure. The S/N ratio of the spectra did become somewhat poorer as the number of carbon atoms (n) increased but not dramatically so, and the authors attributed the gradual reduction to the decreased vapor pressure of the higher molecular weight precursors.

Assignment of the observed spectral bands in the large alkoxy radicals has turned out to be very challenging. Unlike methoxy and ethoxy, larger alkoxy radicals have structural isomers, and the same structural isomer can exist in different conformations. Alkoxy conformers are typically labelled according to whether the non-H substituents are *gauche* (G) or *trans* (T) with respect to one another for each of the C—C bonds in the molecules, (with the C—C bond labelled 1 being the one that is closest to the O atom) (Fig. 1).

The spectral positions of structural isomers are usually wellseparated but those of conformers are not. Indeed, closelyspaced vibronic bands can be expected from the various conformers, e.g., an origin band from one conformer can lie close to a C-O stretch band belonging to an entirely different conformer of the radical. Gopalakrishnan et al. (18) made significant progress analyzing the rotationally resolved $\tilde{B} - \tilde{X}$ LIF spectra of all the strong bands of 1-propoxy. Five vibronic bands were unambiguously assigned to two conformers (G and T). Experimental rotational constants for both \tilde{X} and \tilde{B} states as well as components of the electron spin-rotation tensor in the \tilde{X} state were determined for each conformer. Similar rotational analyses (19) were recently published for 1-butoxy and 1-pentoxy, again correlating the strongest spectral lines with specific conformers.

The method used in the 1-propoxy, 1-butoxy, and 1-pentoxy analyses is computationally intensive (18, 19). It involves identifying all likely stable conformations using the systematic pseudo-Monte Carlo (SPMC) methods (20) available in Macro-Model (21). This is followed by quantum chemistry calculations for both the \tilde{X} and \tilde{B} states, optimizing each of these geometries to predict rotational constants. Components of the ground-state electronic spin – molecular rotation tensor were also predicted by a semiempirical method using the experimentally observed spin-rotation tensor of ethoxy as a reference. Finally, comparisons between molecular constants obtained experimentally and those from the calculations are used to identify the carrier of a given band.

When one examines larger open-chain, primary alkoxies, the number (19) of conformers expected (41 for 1-hexoxy, 122 for 1-heptoxy) becomes so large that the computations described above become infeasible. In this paper, we suggest a new technique, which lets us select a candidate conformer for a given band based only upon a comparison of the given experimental spectra with those of smaller alkoxy radicals. Using this ap-



Fig. 2. LIF excitation spectra of the primary alkoxy radicals ($C_nH_{2n+1}O$) from n = 3 - 10. Persistent lines in the spectrum are marked A, B, and C. Conformationally assigned bands are labeled (G for gauche, T for trans) (18, 19) according to the various dihedral angle minima. Excited vibrational levels are indicated as subscripts by their approximate motion, e.g., CO (stretch), CCO (bend), etc.

proach, four conformers were assigned for five vibronic bands of 1-hexoxy and two conformers for three vibronic bands of 1-heptoxy. Extending the analysis to even larger alkoxy radicals is also discussed.

2. Experimental

The alkoxy radicals were generated in a supersonic free jet expansion by UV laser photolysis (XeF) of the corresponding alkyl nitrites at the base of a 0.5 mm circular nozzle. The alkyl nitrites were synthesized according to well-known procedures (22). A few torr (1 torr = 133.322 Pa) of the alkyl nitrite vapor was entrained into the jet flow by passing helium at 6 atm (1 std atm = 101.325 kPa) over the liquid contained in a steel bomb maintained at a suitable temperature depending upon the vapor pressure.

The rotationally resolved LIF spectra of the 1-alkoxy radicals were obtained on our high-resolution apparatus, which has been described elsewhere (23). Briefly, a cw ring dye laser (Coherent 899-29 Autoscan) pumped by an Ar⁺ laser (Coherent Innova Sabre) was pulse amplified and frequency doubled using a KDP crystal to generate the UV radiation required to



Fig. 3. Rotationally resolved spectra of primary alkoxy radicals from 1-propoxy to 1-heptoxy: (a) band A, (b) band B, and (c) band C.

pump the $\tilde{B} - \tilde{X}$ transition of the alkoxy radicals. The pulse amplifier (Lambda Physik, FL 2003 model) was pumped by an excimer laser (XeCl, Lambda Physik, MSC 103 model) with a resulting line width of ≈ 100 MHz in the fundamental (200 MHz when doubled into the UV). This radiation was directed into a vacuum chamber ≈ 15 mm downstream of the nozzle orifice to excite the $\tilde{B} - \tilde{X}$ transition. The resulting fluorescence was collected perpendicular to the probe laser beam with a 2.5 cm f/1 lens. The light was then focused with a f/3 lens through an adjustable slit onto a photomultiplier tube (PMT). The slit can be adjusted to allow only the central portion of the fluorescence from the jet to be detected by the PMT, thereby reducing the Doppler width of the signal from off-axis velocity components in the jet expansion. This signal was then preamplified and sent to a boxcar averager (Stanford Research, SR250 boxcar) for integration. The amplified signal was then sent to the Coherent Autoscan unit for signal averaging and recording.

3. Theory

The theory upon which the analysis of the rotational structure of the bands is based is described in detail in ref. 18, hence only a brief description will be provided here. An asymmetric top Hamiltonian is used to model the rotational structure of the high-resolution electronic spectra of the primary alkoxy radicals. Because of the very low temperature in the jet, only



the lowest few rotational states are populated. Therefore, centrifugal terms in the rotational Hamiltonian (\mathcal{H}_{Rot}) may be neglected. However, the spin-rotation coupling certainly needs to be considered. Hence, the total Hamiltonian can be written:

$$[1] \qquad \mathcal{H} = \mathcal{H}_{Rot} + \mathcal{H}_{SR}$$

In which

$$[2] \qquad \mathcal{H}_{Rot} = AN_a^2 + BN_b^2 + CN_c^2$$

$$[3] \qquad \mathcal{H}_{SR} = \frac{1}{2} \sum_{\alpha\beta} \epsilon_{\alpha\beta} (N_{\alpha} S_{\beta} + S_{\beta} N_{\alpha})$$

where **N** and **S** are the molecular rotational and electron spin angular momentum, respectively. *A*, *B*, and *C* are the rotational constants, and $\epsilon_{\alpha\beta}$ are the components of the spin-rotation tensor in the inertial axis system (*a*, *b*, *c*).

The matrix elements of the Hamiltonian of a nonrigid, nonlinear, polyatomic molecule in a multiplet electronic state have been derived by Raynes (24), and these were programmed into a graphical user interface program SpecView, which was developed in our laboratory (25) to model the spectra of the alkoxy radicals.

The six rotational constants, namely, A'', B'', and C'' in the ground state and A', B', and C' in the excited \widetilde{B} state, need to be fit to the spectra. For the spin-rotation interaction,

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29 648

29 647

only ground-state constants need to be fitted because the spinrotation interaction in the excited state causes splittings unresolvable with the experimental resolution, as confirmed by the study of ethoxy (14). According to Brown et al. (26), six unique spin-rotation constants can be determined for molecules with C1 symmetry, while only four can be determined for molecules with C_s symmetry. In the general case, the spin-rotation constants that can be determined for a single isotopic species are given below in terms of their relationship to the components of the reduced spin-rotation tensor $\tilde{\epsilon}$ introduced by Brown et al.:

Band C

29 646

29 645

$$T_0^0(\tilde{\varepsilon}) = (-1/\sqrt{3})(\tilde{\varepsilon}_{aa} + \tilde{\varepsilon}_{bb} + \tilde{\varepsilon}_{cc}) = \sqrt{3}a_0$$

$$T_0^1(\tilde{\varepsilon}) = (-1/\sqrt{2})i(\tilde{\varepsilon}_{cb} - \tilde{\varepsilon}_{bc}) = 0$$

$$T_{\pm 1}^1(\tilde{\varepsilon}) = (1/2)[(\tilde{\varepsilon}_{ba} - \tilde{\varepsilon}_{ab}) \pm (\tilde{\varepsilon}_{ca} - \tilde{\varepsilon}_{ac})] = 0$$

$$T_0^2(\tilde{\varepsilon}) = (1/\sqrt{6})(2\tilde{\varepsilon}_{aa} - \tilde{\varepsilon}_{bb} - \tilde{\varepsilon}_{cc}) = \sqrt{6}a$$

$$T_{\pm 1}^2(\tilde{\varepsilon}) = \pm (1/2)[(\tilde{\varepsilon}_{ba} + \tilde{\varepsilon}_{ab}) \pm (\tilde{\varepsilon}_{ca} + \tilde{\varepsilon}_{ac})] = \pm (d \pm ie)$$

$$T_{\pm 2}^2(\tilde{\varepsilon}) = (1/2)[(\tilde{\varepsilon}_{bb} - \tilde{\varepsilon}_{cc}) \pm (\tilde{\varepsilon}_{bc} + \tilde{\varepsilon}_{cb})] = (b \mp ic)$$

1-Heptoxy

29 650

29 649

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Constants (GHz)	Band A ^a	Band B^b	Band C ^c	Band \mathbf{B}_a^d	Band C_b^{e}
<i>A</i> ″	8.884(3)[9.062]	12.817(13)[13.549]	13.633(8)[13.549]	7.741(19)[7.704]	8.322(23)[8.561]
B''	0.833(1)[0.818]	0.767(1)[0.728]	0.748(1)[0.728]	0.996(3)[0.853]	0.844(6)[0.825]
C''	0.770(1)[0.788]	0.697(1)[0.709]	0.722(1)[0.709]	0.909(3)[0.802]	0.830(6)[0.789]
$\widetilde{\epsilon}''_{aa}$	-0.34(1)[-0.41]	-3.41(6)[-3.82]	-4.08(4)[-3.82]	-0.33(6)[-1.44]	-3.14(30)[-2.70]
$\widetilde{\epsilon}_{bb}^{\prime\prime\prime}$	-0.19(1)[-0.19]	-0.17(1)[-0.04]	-0.01(1)[-0.04]	-0.22(19)[-0.13]	-0.00(21)[0.01]
$\widetilde{\epsilon}_{cc}^{\prime\prime}$	-0.10(1)[-0.05]	0.02(0)[-0.00]	$\cdots [-0.00]$	···[-0.01]	-0.07(21)[-0.01]
$ \widetilde{\epsilon}_{ab}^{''} = \widetilde{\epsilon}_{ba}^{''} $	[0.50]	···[1.00]	· · · [1.00]	\cdots [0.72]	[0.35]
$ \widetilde{\epsilon}_{ac}^{''} = \widetilde{\epsilon}_{ca}^{''} $	$\cdots [0.27]$	$\cdots [0.04]$	$\cdots [0.04]$	· · · [0.19]	[0.34]
$ \widetilde{\epsilon}_{bc}^{''} = \widetilde{\epsilon}_{cb}^{''} $	$\cdots [0.10]$	$\cdots [0.00]$	\cdots [0.00]	[0.03]	· · · [0.01]
A'	8.142(2)[8.501]	12.974(8)[12.807]	12.474(3)[12.807]	7.149(9)[7.287]	8.193(11)[8.624]
B'	0.836(1)[0.837]	0.745(1)[0.738]	0.746(1)[0.738]	0.926(2)[0.869]	0.847(4)[0.827]
C'	0.792(1)[0.802]	0.715(1)[0.716]	0.729(1)[0.716]	0.966(2)[0.814]	0.815(5)[0.793]
$T_0 ({ m cm}^{-1})$	28 636.60(1)	28 989.34(1)	29 662.05(1)	28 983.21(1)	29658.59(1)
Relative energies (cm ⁻¹)	· · · [0.0]	[57]	[57]	[369]	[377]

Table 1. Experimentally determined and calculated (in brackets) values of molecular constants for several conformers of 1-hexoxy.

^{*a*}(G₁T₂T₃T₄) 116 lines assigned, $\sigma = 43$ MHz.

^b(T₁T₂T₃T₄) 129 lines assigned, $\sigma = 121$ MHz.

^c(T₁T₂T₃T₄) 111 lines assigned, $\sigma = 35$ MHz.

 $^{d}(T_{1}T_{2}G_{3}T_{4})$ 116 lines assigned, $\sigma = 194$ MHz.

 $^{e}(T_{1}T_{2}T_{3}G_{4})$ 60 lines assigned, $\sigma = 91$ MHz.

Table 2. Experimentally determined and calculated (in brackets) values of molecular constants for several conformers of 1-heptoxy.

Constants (GHz)	Band A ^a	Band B^b	Band C^c
<i>A</i> ″	7.496(6)[7.492]	11.674(32)[11.716]	11.738(26)[11.716]
<i>B</i> ″	0.530(4)[0.542]	0.512(2)[0.489]	0.484(1)[0.489]
<i>C</i> ″	0.518(4)[0.525]	0.492(3)[0.479]	0.489(1)[0.479]
$\widetilde{\epsilon}_{aa}^{\prime\prime}$	-0.08(4)[-0.35]	-3.79(4)[-3.47]	-3.49(5)[-3.47]
$\widetilde{\epsilon}_{bb}^{\prime\prime\prime}$	-0.01(2)[-0.13]	0.00(9)[-0.03]	[-0.03]
$\widetilde{\epsilon}_{cc}^{''}$	0.00(2)[-0.06]	-0.05(9)[0.00]	[0.00]
$ \widetilde{\epsilon}_{ab}^{''} = \widetilde{\epsilon}_{ba}^{''} $	··· [0.41]	[0.85]	··· [0.85]
$ \widetilde{\epsilon}_{ac}^{''} = \widetilde{\epsilon}_{ca}^{''} $	··· [0.22]	[0.03]	[0.03]
$ \widetilde{\epsilon}_{bc}^{''} = \widetilde{\epsilon}_{cb}^{''} $	••• [0.07]	···· [0.00]	· · · [0.00]
A'	6.872(4)[7.120]	11.085(9)[11.354]	11.124(9)[11.354]
B'	0.548(3)[0.554]	0.503(3)[0.495]	0.493(1)[0.495]
C'	0.526(3)[0.534]	0.502(3)[0.484]	0.491(1)[0.484]
$T_0 ({\rm cm}^{-1})$	28 635.10(1)	28975.04(1)	29647.11(1)
Relative energies (cm ⁻¹)	···· [0.0]	[56]	[56]

^{*a*}(G₁T₂T₃T₄T₅) 109 lines assigned, $\sigma = 116$ MHz. ^{*b*}(T₁T₂T₃T₄T₅) 71 lines assigned, $\sigma = 66$ MHz.

^c(T₁T₂T₃T₄T₅) 69 lines assigned, $\sigma = 75$ MHz.

The parameters a₀, *a*, *b*, *c*, *d*, and *e* were defined by Raynes (24) and because of their notational convenience are used in our spectral analysis.

The prediction of rotational constants was performed via calculations using the Gaussian98 program (27) at the B3LYP/6-31+G* and the CIS/6-31+G* levels for the \tilde{X} and \tilde{B} states, respectively. As already mentioned in the *Introduction*, a semiempirical approach based upon the knowledge of the experimentally determined spin-rotation constants of the ethoxy radical was used to estimate the spin-rotation constants (28).

4. Results

The number (*N*) of conformers grows rather dramatically according to the formula (19), $N = \frac{3^{n-2}-1}{2} + 1$, as the number (*n*) of carbon atoms in the alkoxy radical increases. However, the LIF excitation spectra (Fig. 2) show, if anything, fewer features with an increase of *n* instead of more congestion. Our approach to understanding these spectra builds upon corresponding analyses (18, 19) for 1-propoxy, 1-butoxy, and 1-pentoxy for which multiple conformers were "frozen out" in the jet. For these

Fig. 4. Rotationally resolved band C of 1-hexoxy: (*a*) experimental spectrum, (*b*) simulation using only calculated rotational constants of conformer $T_1T_2T_3T_4$, (*c*) simulation including spin-rotation component $a_0 + a/2$, and (*d*) spectrum simulated from fit constants of Table 1. The ratio of the electric dipole moments a:b:c for the simulation is 0:0:1. The rotational temperature is 1.2 K.



species, detailed spectroscopic analyses determined rotational and spin-rotation constants for two of two 1-propoxy conformers, three of a possible five 1-butoxy conformers, and five of 14 possible conformers of 1-pentoxy.

Figure 2 also shows that there are three bands that appear persistently for all the alkoxy radicals, labelled bands A, B, and C. Interestingly, for 1-propoxy, 1-butoxy, and 1-pentoxy, band B is always correlated with the all-trans conformer, which uniquely has C_s symmetry. Band B has been assigned as the origin band of the $T_1T_2...T_{n-2}$ conformer with all the bands C being assigned as the C-O stretch vibrational fundamental of the same conformer. Similarly, all A bands are assigned to the $G_1T_2...T_{n-2}$ conformer, which retains the C_s symmetry of the carbon chain but has the oxygen rotated 60° out of the carbon-chain plane. The structures of these conformations are illustrated in Fig. 1.

Figure 2 shows that nearly all the strong bands in the spectra of pentoxy and smaller alkoxy radicals have been assigned to specific conformers and their vibronic structure. Figure 3 compares the rotational structure for bands A, B, and C for the alkoxy radicals ($C_nH_{2n+1}O$) with $3 \le n \le 7$. Figure 3 shows, as expected, that the rotational structure becomes increasingly compressed as the molecule increases in size and its rotational constants concomitantly decrease. However, allowing for this compression, we see clearly a great deal of similarity in structure in each labelled band for all the alkoxy radicals. Previous detailed assignments for the propoxy, butoxy, and pentoxy radicals helped guide our present assignments. Based upon the absolute and relative positions of the lines relative to the smaller alkoxies, it seems very reasonable to assign bands B and C to the origin and first C-O stretch of the conformer with C_s symmetry (in 1-hexoxy and 1-heptoxy $T_1T_2T_3T_4$ and $T_1T_2T_3T_4T_5$, respectively), while band A is assigned to the origin of the conformer with the oxygen out of the C_s plane (G₁T₂T₃T₄ and $G_1T_2T_3T_4T_5$ for 1-hexoxy and 1-heptoxy, respectively).

Ab initio calculations were performed for these two conformers for both 1-hexoxy and 1-heptoxy, and the calculated molecular constants are given in Tables 1 and 2 and were used





as a starting point for a full rotational analysis. Details of the analysis are given below for bands A and C of 1-hexoxy. The assignments of other bands were performed in a similar manner.

Figure 4 shows the experimental trace of band C and the simulation of the $\tilde{B} - \tilde{X}$ transition using the rotational constants from the ab initio calculations of conformer $T_1T_2T_3T_4$ of 1-hexoxy. As the $T_1T_2T_3T_4$ conformer has C_s symmetry, only a *c*-type transition dipole is allowed, making the structure of band C (or B) rather simple. The simulation in Fig. 4*b* clearly resembles the experimental spectrum (trace *a*). The P and R branches of the $K'' = 0 \leftrightarrow K' = 1$ transition can be easily identified and assigned although there are clearly small discrepancies between the experimental and simulated structure. The positions of the Q branch for $K'' = 0 \leftrightarrow K' = 1$ as well as $K'' = 1 \leftrightarrow K' = 0$ and $K'' = 1 \leftrightarrow K' = 2$ can easily be located, but the latter two appear as doublets experimentally. At this stage, combinations of rotational constants, (B + C)/2 and A - (B + C)/2 of the ground state and (B + C)/2 of the excited \tilde{B} state, can be fitted.

The splitting between the doublets of the Q branches is about 2.2 GHz. It is close to the calculated splitting of 2.6 GHz $[3/2(a_0 + a/2)]$ for transitions involving |K''| = 1and N'' = 1, due to the spin-rotation interaction in the ground \tilde{X} state. Smaller splittings are observed in the P($K'' = 0 \Leftrightarrow$ K' = 1) and R($K'' = 0 \Leftrightarrow K' = 1$) branches (but not completely resolved); these observations are consistent with the calculated value of 0.06 GHz for transitions involving K'' = 0, which are split by the term $(N'' + 1/2)(a_0 - a)$.

Simulations including the calculated spin-rotational component $a_0 + a/2$ (Fig. 4c) enabled us to assign most of the remaining experimental lines. At this point, least-square fits of 111 lines were used to determine the origin frequency, \widetilde{X} and \widetilde{B} state rotational constants, and the two most significant \widetilde{X} state spinrotation tensor components ($\widetilde{\epsilon}_{aa}, \widetilde{\epsilon}_{bb}$). The simulation based upon this fit is given in Fig. 4d and the corresponding molecular parameters are listed in Table 1. Good agreement is seen between the experimental results and values from the ab initio calculations. For the rotational constants, the values are within $\pm 5\%$ for both ground and excited states. For the spin-rotation constants, the values were within 7% for the larger component, $\tilde{\epsilon}_{aa}^{\prime\prime}$. Several of the spin-rotation constants could not be determined experimentally because the effect they had on the spectrum was below the experimental resolution ($\approx 200 \text{ MHz}$). In this case, those spin-rotation constants were fixed at zero in the fitting.

Band B was assigned according to the same procedure as described for band C. Its analysis was made after the assignment of band C because there was another band partially overlapping it (Fig. 3b). The overlap will be discussed later in this paper. In spite of the overlap, unambiguous assignments can still be made and the resulting parameters are listed in Table 1.

As noted in the beginning of this section, the likely assignment for band A is to conformer $G_1T_2T_3T_4$. The structure of band A appears more complicated than that of bands B and C because conformer $G_1T_2T_3T_4$ only has C_1 symmetry rather than

Fig. 6. Survey LIF spectra of 1-hexoxy and 1-heptoxy. Expanded views of the regions of bands B and C show additional lines in the 1-hexoxy spectrum, but not in the 1-heptoxy spectrum.



 C_s symmetry as for the T₁T₂T₃T₄ conformer. There are now three nonzero components of the transition dipole rather than one. The increase in allowed transitions leads to increased spectral congestion, making the spectral analyses somewhat more difficult.

However, the analysis of bands B and C and other alkoxy bands in our previous work (18,19) indicated that ab initio predictions of the molecular constants should be quite reliable. Indeed, the simulation using the calculated molecular constants of conformer G1T2T3T4 shows rather good agreement with the experimental spectrum of band A (Fig. 5b). Nonetheless, the spectral congestion makes it difficult to distinguish the rotational and spin-rotation splittings in the center of the band. The spinrotation splitting is more easily discerned at the ends of the spectrum where higher N'', |K''| > 0 transitions lie. By including the calculated value of the spin-rotation constants $\widetilde{\epsilon}_{aa}''$ and $\widetilde{\epsilon}_{bb}''$ in the simulation, all the doublets at the ends of the experimental spectrum are accounted for in the simulation (Fig. 5c). Then assignments can be made for branches $Q(K'' = 1 \leftrightarrow K' = 2)$, $R(K'' = 2 \leftrightarrow K' = 3)$, and $Q(K'' = 2 \leftrightarrow K' = 1)$. Using these assignments, an initial fit can be made to obtain experimental rotational constants and spin-rotation components, and the resulting simulation is shown in Fig. 5d. At this stage, more lines in Q($K'' = 2 \leftrightarrow K' = 3$), R($K'' = 1 \leftrightarrow K' = 2$), $P(K'' = 1 \leftrightarrow K' = 0)$, and $R(K'' = 0 \leftrightarrow K' = 1)$ branches can be assigned. The final fit was then performed with all the off-diagonal spin-rotation components fixed at zero. The resulting simulation is shown in Fig. 5*e*, and the corresponding molecular constants are listed in Table 1.

For 1-heptoxy, band A is assigned to conformer $G_1T_2T_3T_4T_5$ despite the increasing congestion in the rotationally resolved spectrum. For bands B and C, overlap with an additional band makes the structure even more complicated. However, a reasonable fit can still be made for the $T_1T_2T_3T_4T_5$ conformer portion of the spectrum using the same approach as for the 1-hexoxy analysis. The results are given in Table 2.

Bands from additional conformers were identified in 1-butoxy and 1-pentoxy. The bands identified included the origin of the T_1G_2 conformer of 1-butoxy, the origin of the $T_1T_2G_3$ and T₁G₂T₃ conformers of 1-pentoxy, and the C-O stretch bands of the T₁T₂G₃ and T₁T₂T₃ conformers of the 1-pentoxy spectrum. In addition, low-frequency fundamentals and combination bands of these conformers appeared in the spectra. The additonal conformers observed in 1-butoxy and 1-pentoxy all have a nearly straight chain structure obtained by rotating one C-C-C dihedral angle of the C_s (all-trans) conformer. One expects that bands of this nature will shift closer to each other in 1-hexoxy as the difference between these conformers becomes less significant with the increasing length of the carbon chain. The expanded region in Fig. 6 of the 1-hexoxy LIF spectrum shows one extra band (B_a) close to band B and two extra bands $(C_a \text{ and } C_b)$ close to band C. From 1-heptoxy to 1-decoxy, there is no clear separation between these bands, implying they might completely overlap. An expanded view of the 1-heptoxy



Fig. 7. Simulations using the calculated constants of the $T_1T_2T_3G_4$, $T_1T_2G_3T_4$, and $T_1G_2T_3T_4$ conformers of 1-hexoxy, as well as rotationally resolved experimental spectra of additional bands of 1-hexoxy close to bands B and C.

Fig. 8. Comparison of experimental rotationally resolved spectra of band C_b (top) and B_a (bottom) with their respective simulations using the constants from Table 1.



Frequency (cm^{-1})

LIF spectrum in the band B and C region only shows a single band, but the rotationally resolved spectra of each band displays overlap with an additional transition.

High-resolution spectra of bands B_a , C_a , and C_b were obtained and are shown in Fig. 7. Of the 41 conformers of 1-hexoxy, there are three conformers derived from the all-trans T conformer by changing only one C-C-C dihedral angle, i.e., $T_1T_2T_3G_4$, $T_1T_2G_3T_4$, and $T_1G_2T_3T_4$. Simulations using the computed rotational constants (Fig. 7) indicated that the $T_1T_2T_3G_4$ conformer yields the closest match for band C_b , and the $T_1T_2G_3T_4$ conformer for B_a . Results of fits to these are given in Fig. 8 and Table 1. There is no obvious conformer assignment for band C_a .

Band B_a is assigned as the origin band of conformer $T_1T_2G_3T_4$, as no band with comparable intensity was assigned below this frequency. A definite vibrational assignment cannot be made for band C_b , although it appears in the C-O stretch frequency region. A band partially overlapped with band B appearing in the rotationally resolved spectrum might be the buried origin of the $T_1T_2T_3G_4$ conformer, but an unambiguous assignment cannot be made due to the low signal-to-noise ratio and the congestion.

With these results in hand, we can return to the spectra of 1-octoxy, 1-nonoxy, and 1-decoxy in Fig. 2. As with 1-hexoxy, 1-heptoxy, and the smaller alkoxies, it is easy to identify bands A, B, and C. We have not attempted to obtain rotationally resolved spectra of these bands to obtain a definitive conformational assignment. Nonetheless, we feel that the close analogy between the 1-octoxy to 1-decoxy spectra in Fig. 2 and the spectra of the smaller alkoxies leaves little doubt as to the conformational assignments. It appears highly probable that band A is the origin of the $G_1T_2...T_{n-2}$ conformer, while bands B and C are, respectively, the origin and CO stretch fundamental of conformer $T_1T_2...T_{n-2}$. One would also expect this pattern to continue in even larger alkoxy radicals.

5. Conclusions

Rotationally resolved spectra of six bands of 1-hexoxy and three bands of 1-heptoxy were obtained. A new strategy was used for the analysis of the 1-hexoxy and 1-heptoxy spectra and is applicable for larger primary alkoxy radicals. Using this approach, five bands of 1-hexoxy were assigned to four different conformers, i.e., band A to $G_1T_2T_3T_4$, bands B and C to $T_1T_2T_3T_4$, band B_a to $T_1T_2G_3T_4$, and band C_b to $T_1T_2T_3G_4$. For 1-heptoxy, band A was assigned to conformer $G_1T_2T_3T_4T_5$, while bands B and C were assigned to conformer $T_1T_2T_3T_4T_5$. Experimental molecular parameters were obtained from the rotational analyses, which are in rather good agreement with the values predicted for the given conformers by quantum chemistry calculations.

In earlier work (29, 30), probing a jet-cooled sample via microwave spectroscopy, it was suggested that little conformation relaxation takes place from the room-temperature conformer distribution. This work includes studies on 1-pentene and 1-hexene, which of course bear similarities to the presently studied alkoxies. However, with the alkoxy radicals there is an important difference in that they are created by photolysis in the jet.

Our earlier work on smaller alkoxies reached the conclusion (18, 19) that multiple conformers exist in the cold-jet environment, i.e., the sample is not at thermal equilibrium with the rotational temperature — indeed the conformers do not appear to form an equilibrium distribution for any temperature. However, the conformers are not all populated. The bands assigned arise from all-trans conformers or conformers with at most one gauche linkage. Three bands, the $T_1T_2...T_{n-2}$ origin and CO stretch and the $G_1T_2...T_{n-2}$ origin, form the main "structure" of the LIF spectra of large primary alkoxy radicals. The origin, and occasionally the CO stretch fundamental bands from other nearly straight chain conformers, "decorate" the spectra and coalesce into the three dominant bands as the number of carbons in the radicals increases.

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