Electronic Spectroscopy of CF₃O in a Supersonic Jet: Symmetry and Rotational Structure of a Prototypical Perfluoroalkoxy Radical

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The $\tilde{A} \leftarrow \tilde{X}$ electronic transition of CF₃O was observed in a supersonic jet using laser-induced fluorescence. Rotational analysis of the high-resolution spectrum of the origin band is consistent with CF₃O having C_{3v} symmetry in both its ground and excited electronic states. The lowest level is best described as ${}^{2}E_{3/2}$ with residual unquenched electronic angular momentum, leading to a significant spin-orbit splitting.

Introduction

The geometry and electronic structure of the prototypical perfluoroalkoxy radical, CF_3O , has considerable theoretical interest, especially in comparison to the by now relatively well-studied¹⁻⁴ methoxy radical, CH_3O . It also has potential significance in atmospheric chemistry; CF_3O is one of the intermediates in the degradation of the hydrofluorocarbons (HFCs) in the upper atmosphere.⁵ Since the HFCs are potential replacements for the ozone-depleting chlorofluorocarbons (CFCs), there has been an explosive interest⁶⁻¹³ in the study of the reaction rates of CF_3O , as part of the effort to understand the environmental impact of the HFCs. The spectroscopy of CF_3O can play a key role both in unraveling the radical's structure and bonding and in monitoring its chemical reactions.

The spectroscopic and structural work on CF₃O was largely initiated by Francisco and co-workers. They performed a series of theoretical and experimental studies¹⁴⁻¹⁶ on this radical. They reported the $\tilde{A} \leftarrow \tilde{X}$ electronic transition of CF₃O with an origin at 28 478 cm⁻¹ and made vibrational assignments in both the ground and the excited electronic states with the aid of ab initio calculations. Their experimental observations were mostly confirmed by Saathoff and Zellner¹⁷ in a recent study. Unfortunately, both studies suffer from relatively poor spectral resolution and congestion since the experiments were carried out at ambient temperature. Consequently, it was impossible to definitely determine from the spectra whether the symmetry of the radical is C_{3v} or C_s in its ground electronic state. In a similar fashion, the results of *ab initio* calculations have oscillated between a C_{3v} geometry¹⁶ or a distortion to C_s geometry,¹⁴ presumably because of Jahn-Teller effects.

We report here the first laser-induced fluorescence (LIF) experiment of CF₃O in which the radical has been cooled by a supersonic free jet expansion. The $\tilde{A} \leftarrow \tilde{X}$ transition of this radical has been studied under both moderate and high spectral resolution, the latter yielding nearly completely resolved rotational structure. As expected, significant new information about this radical was obtained. In particular, from the rotational analysis, the symmetry and the electronic structure of CF₃O in its ground electronic state are greatly clarified.

Experimental Section

 CF_3O was generated by *in situ* ArF excimer laser photolysis of a small percentage of precursor molecules in the free jet

expansion. The precursors used were either trifluoromethyl hypofluorite¹⁸ (CF₃OF) or bis(trifluoromethyl) peroxide¹⁹ (CF₃-OOCF₃). CF₃OF was prepared by a modification of a literature method.²⁰ Dried cesium fluoride (20 g) was placed in a stainless steel cylinder which was then charged with 200 mmol of CF₂O and F_2 at -196 °C. The reaction mixture was allowed to warm slowly from -196 to 22 °C over 5 h. The CF₃OF was purified by removing excess F2 under dynamic vacuum at -196 °C. CF3-OOCF₃ was prepared by passing fluorine (120 cm³/min) and carbon monoxide (80 cm³/min) through a reactor heated to 180-200 °C and containing a catalyst composed of copper ribbon coated with silver difluoride. The crude product was collected in a glass trap at -85 °C and purified by pumping under dyanmic vacuum through a trap cooled to -135 °C. The CF₃OOCF₃ in the -135 °C trap was then passed at 1 atm through 12 N NaOH to remove CO₂, CF₂O, and CF₃OF. This was followed by drying through a column of CaSO₄.

The moderate-resolution LIF apparatus has been described before.²¹ Briefly, CF₃OF or CF₃OOCF₃ was seeded in 100 psig of He, expanded through a pulsed nozzle into vacuum, and photolyzed with an ArF excimer laser at the throat of the jet. The resulting CF₃O was probed 8 mm downstream by an excimer pumped dye laser beam, frequency doubled with an external KDP crystal. The excitation spectrum was obtained by collecting fluorescence and imaging it onto a photomultiplier. The wavelength-resolved emission spectrum was obtained by imaging the fluorescence onto a monochromator and detecting the dispersed fluorescence by a diode array detector. Two different dyes, OX720 and LD690, were used to cover the frequency region of 28 500– 29 900 cm⁻¹.

The high-resolution LIF apparatus has also been described before.²² The experimental procedure is similar to that used in the moderate-resolution experiment. The pulse amplified, frequency-doubled output of a CW ring dye laser (Coherent CR699-29), operating with pyridine 2, was used as the probe source. The pulse amplified probe laser line width is about 125–150 MHz (250–300 MHz doubled) under current operating conditions. The spectrum was calibrated by simultaneously recording etalon fringes of a low finesse (FSR \approx 475 MHz) homemade etalon for relative calibration, and absolute calibration was done by recording a Ne transition (at 28 553.334 cm⁻¹) in an optogalvanic cell.

Results and Discussion

Figure 1 shows the fluorescence excitation spectrum of the origin region of the CF₃O $\tilde{A} \leftarrow \tilde{X}$ transition, with the strong

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28600 28800 29000 29200 29400 29600 29600 cm⁻¹

Figure 1. Fluorescence excitation spectrum of CF_3O $\tilde{A} \leftarrow \tilde{X}$ transition. The band marked by an asterisk has a very different rotational contour from the other bands.

 TABLE 1: Values of the Å State Vibronic Parameters (cm⁻¹)

	ref 15	ref 17	this work
ν ₀₀	28478	28542(28)	28551.7(1)
ω_{a}^{a}	463	410(50)	425(2)
$\omega_{b}{}^{b}$	718°	680(150)	634(2)

^e This vibration was identified^{15,17} as ν_6 , the asymmetric nominal OCF deformation mode. ^b This vibration was identified^{15,17} as ν_2 , the symmetric nominal C–O stretch mode. ^c $\omega_e x_e = -4.5$ cm⁻¹ (ref 15).

origin band centered at 28 552 cm⁻¹. Activity in two vibrational modes of the \overline{A} state are indicated in Figure 1 and labeled v_a and $v_{\rm b}$, respectively. In Table 1, we compare our observations with the two previous LIF studies at room temperature. First, it is important to note that there is good qualitative agreement among all three experiments. The values of v_{00} and the vibrational frequencies are in agreement with those of ref 17 within the latter's (very large) experimental errors. There does appear to be discrepancy between our values and the ones (no specific error limits were given) of ref 15. We expect much of this discrepancy arises from the very broad line contour in the previous room temperature spectra. In Figure 1 there is one observable feature (at 29 177 cm⁻¹, marked by an asterisk) that is not identifiable in terms of the above-mentioned vibrational modes. This band also displays a rotational contour that is distinctly different from those of the other bands in the spectrum. This observation might support the interpretation of this band as arising from a species other than CF₃O. However, we found it appeared with approximately the same relative intensity whether CF₃OF or CF₃OOCF₃ was photolyzed. This band requires further investigation.

We have also observed the dispersed fluorescence spectrum of CF₃O by pumping the 0_0^0 transition. As with the excitation spectrum, the spectrum is qualitatively the same as observed by Li and Francisco¹⁵ and Saathoff and Zellner.¹⁷ Nevertheless, our cold jet spectrum showed much better spectral resolution than earlier observations. In particular, we saw a previously unresolved splitting of the 0_0^0 band of 41 ± 5 cm⁻¹. Like the dispersed fluorescence spectrum of the $\tilde{A}^2A \rightarrow \tilde{X}^2E$ transition of the CH₃O,² several other, but not all, bands in the CF₃O spectrum showed a similar splitting. In CH₃O, this phenomenon was attributed to the spin-orbit splitting of ground electronic state, which is quenched in the levels involving excitation of asymmetric vibrations. A similar explanation is attractive for CF₃O, yielding the conclusion that the transition is from the \tilde{A}^2A state to the ground state, which is ²E in C_{3v} symmetry. However, before embracing that conclusion, we note that the paired lines could arise also from transitions to closely separated A' and A" states, if the radical is distorted to C_s symmetry. Indeed, the complexity of the emission spectrum, if anything, favors the lower C_s symmetry.

To differentiate between these explanations, we obtained the high-resolution spectrum of the origin band of the $\tilde{A} \leftarrow \tilde{X}$ electronic transition, shown in Figure 2. It contains roughly 100,



Figure 2. High-resolution experimental spectrum of the 0_0^0 band of $\tilde{A} \leftarrow \tilde{X}$ transition of CF₃O (trace a). The relative intensities may not be reliable due to the possibilities of changing experimental conditions in the duration (several hours) of recording the spectrum and the unknown degree of spectral saturation. Trace b shows a simulated spectrum of the 0_0^0 band of the $\tilde{A}^2A \leftarrow \tilde{X}^2E_{3/2}$ electronic transition of CF₃O. The rotational temperature is 3.5 K. The molecular parameters used in the simulation were obtained from the fit described in the text and are given in Table 2. Note that, due to the relatively large uncertainty in the intensities, our analysis is based upon the extremely good fit of the line frequencies (see text).

TABLE 2: Molecular Constants^a of CF₃O (cm⁻¹)

<u></u>	this work	ab initio ^b
Σ ² E		
A	0.19568°	0.19568
В	0.19821(5)	0.20188
ased	$-41(5)^d$	
$A\zeta_t - \epsilon_{aa}/4$	0.05535(8)	
òA		
A	0.19715 ^c	0.19725
В	0.19527(5)	0.19819
origin ^e	28531.220(3)	

^a Numbers in parentheses are one standard deviation. ^b Calculated from the results (at UHF/6-31G* level) of ref 16. ^c The A constants cannot be uniquely determined in the current study. Therefore, the ground-state A constant is fixed at the *ab initio* value. ΔA is determined to be 0.001 48(4) cm⁻¹. ^d Fixed at the value measured from the dispersed fluorescence spectrum. ^e The origin listed in this table is not at the center of the observed band. It is the origin of the ground-state spin-orbit doublet, assuming $a\zeta_{c}d$ is exactly -41 cm⁻¹.

mostly resolved transitions and spans about 6 cm⁻¹. The fwhm of a single line is about 300 MHz, which is primarily limited by the laser line width and residual Doppler broadening. The spectrum shows no simple structure that allows immediate identification of the rotational band type, probably due to CF₃O being nearly a spherical rotor. Careful study of the spectrum resulted in the identification of several rotational progressions. Using the rotational constant B, calculated from *ab initio* geometry,¹⁶ these progressions could be classified into the 1B and the 3B progressions (i.e., adjacent members separated by 1B and 3B, respectively, in frequency). This suggests^{22,23} that a ${}^{2}A \leftarrow$ ²E type of transition is required to interpret the spectrum. Further analysis was then focused on fitting the spectrum with this model. After some iterations the spectrum was satisfactorily fit, using the same Hamiltonians as employed for methoxy.^{1,2,24} The number of transitions included in the final least-squares analysis was 96. The standard deviation of the fit was 50 MHz, very acceptable as compared to the 300-MHz spectral line width. A simulated spectrum is plotted underneath the experimental spectrum in Figure 2b. In all cases, the line positions agree very well between the two although the reproduction of the experimental intensity is less than perfect, because of experimental difficulties in obtaining the true relative intensities. The molecular constants of CF_3O are listed in Table 2 along with those calculated from Francisco et al.'s ab initio geometries.16

The identification of the ground electronic state as ${}^{2}E$ in the $\tilde{A} \leftarrow \tilde{X}$ transition is rather clear. Similar to the diatomic ${}^{2}\Sigma \leftrightarrow$ ²II transitions,²⁵ the 1B and 3B progressions are characteristic of transitions between rotational levels described by integral Nquantum numbers (for a ²A state) and those described by half odd integral J quantum numbers (for a ${}^{2}E_{3/2}$ state). If the $\bar{A} \leftarrow$ \tilde{X} transition is that of $A' \leftarrow A''(A')$, one would expect 2B, rather than 1B and 3B progressions, since both electronic states can be described by integral N quantum numbers. The rotational levels described by half odd integral J quantum numbers result from a significant spin-orbit splitting in the degenerate ²E state. Therefore, the 41-cm⁻¹ splitting observed in the dispersed fluorescence spectrum is indeed spin-orbit splitting. This indicates that the unpaired electron has significant unquenched orbital angular momentum in the ground state.

We can also gain some insight into the degree of electron orbital angular momentum quenching using the result of $a\zeta_c d = -41$ cm⁻¹ from the spin-orbit splitting. To interpret this value, it is useful to compare with the results for methoxy. In CH₃O, $a\zeta_e d$ = -62 cm⁻¹, a = -146 cm⁻¹, and therefore $\zeta_{ed} = 0.43$. If we assume similar C–O bonding in CF_3O , a should be approximately the same, and we obtain $\zeta_e d \approx 0.28$. This indicates substantial quenching of the electronic orbital angular momentum by the Jahn-Teller distortion. On the other hand, the orbital angular momentum is far from completely quenched as would be expected if the radical were permanently distorted to C_s symmetry.

A similar result is obtained when one considers the value of ζ_t . From the rotational analysis, $A\zeta_t - (\epsilon_{aa})/4 = 0.0554 \,\mathrm{cm}^{-1}$. We could expect $\epsilon_{aa}/4 \sim -0.013$ cm⁻¹ by scaling the corresponding value of methoxy² with respect to the A rotational constants. This yields $\zeta_t \sim 0.22$, smaller but again comparable to the methoxy value ($\zeta_t = 0.35$).

CF₃O was previously considered to have C_s symmetry in its ground electronic state, based on ab initio calculations^{14,26} and the many vibrational transitions observed in the dispersed fluorescence spectrum.^{15,17} However, the totality of our evidence is that the ground-state geometry of CF_3O is, like that of CH_3O , best described by C_{3v} symmetry. Semiquantitatively, the Jahn-Teller distortion appears greater in CF₃O, evidenced by greater angular momentum quenching and the appearance in the emission spectrum of several strong bands apparently ending on levels involving excitation of asymmetric vibrational modes.

Because of the coldness of the jet, we have obtained thus far only a high-resolution spectrum for the lowest spin-orbit component $({}^{2}E_{3/2})$ of the ground state. From this measurement alone, we have determined in some cases only a linear combination of parameters, e.g., $A\zeta_t - (\epsilon_{aa}/4)$, and in some other cases, no measurement at all, e.g., the Jahn-Teller parameters, h_1 , and h_2 . Comparable spectra of the upper ${}^{2}E_{1/2}$ spin-orbit component should go far to eliminating these problems. Such spectra are obtainable either by observing LIF from transitions originated from a more populated ${}^{2}E_{1/2}$ level or by observing stimulated emission spectra to it. Such spectra, coupled with the analysis of our emission spectra, should provide a much more complete description of this radical.

In conclusion, the $\tilde{A} \leftarrow \tilde{X}$ electronic transition of CF₃O has been studied under supersonic jet conditions. The moderate-

resolution fluorescence excitation spectrum and the dispersed fluorescence spectrum reveal the very different vibrational structures in the ground and the excited electronic states. For the first time the ground-state spin-orbit splitting in CF₃O is observed. The separation between the ${}^{2}E_{1/2}$ state and the ${}^{2}E_{3/2}$ states is found to be about 41 cm⁻¹. Rotational analysis of the high-resolution spectrum of the 0_0^0 band shows that the spectrum can be fit to a $\tilde{A}^2 A \leftarrow \tilde{X}^2 E$ transition scheme. This, along with the evidence for unquenched orbital angular momentum in the \tilde{X} state, indicates that CF₃O is describable in terms of C_{3p} geometry in both its ground and excited electronic states. More experiments are needed to fully understand the complicated vibronic and geometric structure of this radical. These investigations are currently underway, and the results will be presented in a future publication.

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