Laser Induced Fluorescence and Fluorescence Depletion Spectroscopy of the Jet-Cooled CF$_3$S Radical

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The spectrum of the CF$_3$S free radical has been observed for the first time cooled in a supersonic free jet expansion. Both "bright" and "dark" levels of the $\tilde{A}$ state have been observed using a combination of laser induced fluorescence and fluorescence depletion spectroscopy. The photofragmentation of CF$_3$S is shown to be very mode specific.
1. Introduction

Methoxy, CH$_3$O,$^{1-9}$ and its F- and S- substituted derivatives, CH$_3$S,$^{10}$ CF$_3$O,$^{11-14}$ and CF$_3$S,$^{15-18}$ form a remarkably fascinating family of free radicals from a number of perspectives. Several members are known, or speculated, to be key intermediates in a number of chemical reactions relevant to combustion$^{15-18}$ and atmospheric pollution.$^{13,19-29}$ Unambiguous spectral information about the radicals is therefore highly desirable for developing methods for their monitoring. From a theoretical perspective, the ground states of these radicals are $^2E$ in $C_{3v}$ symmetry and hence subject to the competitive effects of Jahn-Teller distortion and spin-orbit coupling.$^{2,3}$ Even for the simplest and best studied radical, CH$_3$O, these interactions are not yet completely understood.$^{4,6}$

As the spectroscopy of these species has gradually progressed, their photochemistry has attracted ever increasing interest. The ground state surfaces of the hydrides are known$^{30}$ to contain another minimum corresponding to the isomeric species, CH$_2$XH where X=O or S. The first excited $^2A_1$ state is expected to undergo photofragmentation with at least three channels identified$^{31}$ in the methoxy: CH$_3$+O, CH$_2$+OH, and CH$_2$O+H. Similar photofragmentation channels are expected for the remainder of the family.

In this paper we report the first spectral observation of the heaviest member of the family, CF$_3$S, using the laser induced fluorescence (LIF) technique via the $^2A_1 \leftrightarrow X^2E$ electronic transition. We assign some of the vibrational structure of this transition and show that certain of these levels undergo selective predissociation or fragmentation. We probe the photochemistry of the $^2A$ state using a new experimental technique, fluorescence depletion spectroscopy (FDS).

2. Experimental

The radicals were produced by ArF laser (~600mJ/cm$^2$-pulse on the sample) photolysis of (CF$_3$S)$_2$ (PCR) entrained in a He expansion with a reservoir pressure of 7 atmospheres with
the partial pressure of (CF$_3$S)$_2$ being provided by its vapor pressure at $-70^\circ$C. A General Valve with nominal 0.7 mm diameter opening was pulsed for the expansion. In these experiments, two different configurations of the experimental apparatus were utilized. The first configuration has been described before$^{2,10,14}$ and has been routinely used to record laser excitation and dispersed fluorescence spectra. The probe (excitation) laser (PL) was a Lumonics Hyperdye pumped by a Lambda Physik EMG103MSG excimer laser. To record excitation spectra the dye laser was scanned under computer control and the resulting molecular fluorescence collected by a EMI9659QB photomultiplier tube. Temporal measurements of the fluorescence decay were obtained in this configuration by time resolving the photomultiplier output with a Le Croy 2262 transient digitizer.

The FDS experiments required the more complex experimental arrangement illustrated in Figs 1 and 2. The basis of the FDS experiment rests on the following principles. The probe laser (PL) is fixed at the frequency of a strongly fluorescing transition of the $\tilde{A}$ state, e.g., for these experiments $\nu_3' = 3$. The frequency of the dump laser (DL) is then varied as the total laser induced fluorescence from the $\tilde{A}$ state is monitored by the gated CCD camera. Since the DL, with a near-saturating pulse energy of 3-4 mj focused to a 2 mm spot, is fired approximately 50 nsec before the PL, it will significantly deplete the lower level common to both transitions, i.e., the vibrationless level of the $\tilde{X}$ state, when it is in resonance. If the upper level of the DL transition does not fluoresce appreciably, this transition will appear as a decrease in PL induced fluorescence or a negative-going signal. Should the transition excited by the DL have a strongly fluorescing $\tilde{A}$ state level, the DL and PL excited fluorescence will combine to produce a net increase in detected fluorescence or a positive-going signal just as in an ordinary LIF spectrum. Upper state levels with competitive radiative and non-radiative pathways can appear as either positive- or negative-going signals, depending upon the relative rates of the two processes.

In any laser double resonance experiment a key difficulty is to distinguish between the changes in PL induced fluorescence caused by the presence of a second laser, e.g., in our case the depletion laser, DL, and random fluctuations in fluorescence caused by shot-to-shot
variations in radical production and PL intensity. To cancel the latter effects we split the PL into two equal beams, each of 0.5 mJ energy, focused to \( \sim 1 \text{mm} \) diameter spots in different but equivalent regions of the expansion. As shown in Fig. 2, each of these regions is imaged upon the gated intensified CCD camera which is turned on to coincide with the radical’s fluorescence decay. With the PL fixed on resonance, in the absence of the DL, the image is as shown in Fig. 2. The DL can be overlapped with one of the matched spots of the PL and fired \( \sim 50 \text{nsec} \) prior to the PL. When the scanned DL frequency coincides with a non-fluorescing excited state, the trace labelled \( I_1 \) in Fig. 2 is significantly reduced due to depletion of ground state radicals by DL. We define the signal \( S \) to be given by

\[
S = \frac{I_1}{I_2}
\]

(1)

where \( I_1 \) and \( I_2 \) are the areas of the indicated peaks in Fig. 2.

3. Results and Analysis

Fig. 3 shows the LIF excitation spectrum of CF\(_3\)S over a 2500 cm\(^{-1}\) range from the origin band to the blue. We believe that we have observed activity in five vibrational modes in the spectrum, all three of the totally symmetric \( a_1 \) modes and two of the three doubly degenerate \( e \) modes to which transitions are allowed by Jahn-Teller effects in the \( \tilde{X} \) state. We will defer a detailed analysis of the \( \tilde{A} \) vibrational structure, as well as that of the \( \tilde{X} \) state as revealed by the dispersed fluorescence spectrum, to another publication.\(^{32}\)

Here we restrict ourselves primarily to the progression marked \( \nu_3 \) in Fig. 3, which we attribute approximately to the C-S stretching mode in CF\(_3\)S. The C-X (X=S or O) stretching mode is a long, dominant progression in the previously observed \( \tilde{A}^2A_1 \leftrightarrow \tilde{X}^2E \) excitation spectra of methoxy and some of its derivatives.\(^{2,3,10}\) This progression arises because of a significant weakening of this bond upon electronic excitation which nominally promotes a C-X bonding electron to form a lone pair in a \( \pi \) orbital largely localized on X. Based upon the large difference in their \( \tilde{X} \) and \( \tilde{A} \) frequencies we would again expect the \( \nu'_3 \) progression in CF\(_3\)S to be strong and extensive. While the \( \nu_3 \) mode is easily identified in Fig. 3, it
hardly dominates the spectrum nor is it particularly long; indeed \( \nu'_3 = 4 \) is rather weak and \( \nu'_3 = 5 \) is missing. This observation is particularly surprising since \( \nu'_3 = 5 \) or 6 would be expected to have considerable oscillator strength due to the pronounced weakening of the C-X bond, as was clearly observed in the excitation spectra of CH\(_3\)O and CH\(_3\)S. Since detection of the spectrum requires the molecule to decay by fluorescence from the upper level, a possible explanation for the unexpectedly quick termination of the \( \nu'_3 \) progression might be the opening of one of the previously mentioned photofragmentation channels for CF\(_3\)S in the \( \tilde{A} \) state. However, for this explanation to be correct the photofragmentation must be extremely mode-selective, since Fig. 3 shows strong fluorescence signals in the spectral region where \( \nu'_3 = 5, 6, 7... \) would be expected.

To try to resolve this dilemma we turned to the FDS experiments described in Section 2. Fig. 4 shows a comparison of the LIF and FDS spectra over a selected region of the \( \tilde{A} \) \(^2A_1 \leftrightarrow \tilde{X} \) \(^2E \) transition. The FDS spectrum shows the same (positive-going) features as the LIF spectrum but in addition reveals a number of depletion (negative-going) features not present in the LIF trace. We attribute these new (negative-going) features to “dark”, non-fluorescing vibrational levels of the \( \tilde{A} \) \(^2A_1 \) state of CF\(_3\)S. (A few features which appear weakly in the LIF spectrum also appear as negative features in the FDS trace. We attribute these features to levels where fluorescence and fragmentation occur at comparable rates.)

A couple of features of Fig. 4 merit special note. (i) As the figure shows almost all the features in both the LIF and FDS spectra can be assigned to overtone and combination bands. These assignments rest on extrapolation of vibrational progressions from the much less complex lower frequency regions of the spectrum. The extrapolations are straightforward as the progressions are surprisingly harmonic with only small higher order terms. (ii) From Fig. 4 we also see that photofragmentation is extremely mode-selective, but relatively insensitive to total energy content. For instance, levels involving only fundamentals, overtones, or combinations of \( \nu_1 \) and \( \nu_2 \) seem to be essentially immune to photofragmentation, except at the highest energies investigated. On the other hand, levels with several quanta of \( \nu_3 \) readily photofragment. As mentioned above, \( \nu_3 \) nominally corresponds to the F\(_3\)C-S
symmetric stretch which is the bond that would be broken in what, in analogy with CH₃O, is likely the lowest energy photoproduct channel, CF₃ + S.

For this reason, we have undertaken a systematic study of the lifetimes of the members of the pure ν₃ progression. We note from Fig. 3 that levels ν₃′ = 0 – 4 are observed in the LIF spectrum while levels ν₃′ = 4 – 8 are identified as depletion signals in the FDS spectrum. We have measured the temporal behavior of the fluorescence decay in levels ν₃′ = 0 – 4 and report their values in Table I. We note that for ν₃′ = 0 – 3 the lifetimes, τ, are nearly constant in the range 2.5-3.0 μs. However at ν₃′ = 4, τ abruptly drops to 38 ns. Making what seems the very safe assumption that the radiative lifetime is roughly independent of ν₃′ one deduces that about 99% of the molecules excited to ν₃′ = 4 fragment and only about 1% fluoresce. This latter 1% give rise to the (relatively weak) LIF signal while the 99% lead to the depletion signal.

For levels ν₃′ > 4, no fluorescence is detected but clear FDS signals are seen for ν₃′ = 5 – 8. The FDS traces for ν₃′ = 4 and 5 have a linewidth (FWHM) of 1.0 cm⁻¹ which is narrower than the rotational contour (2-3 cm⁻¹) of the LIF signals of transitions to nearby fluorescing states. (Presumably, this arises from the selective excitation by the PL of only some of the rotational levels populated.) The ν₃′ = 6 level is so overlapped with another transition that measurement of its width is not possible. The ν′ = 7 and 8 FDS lines also are somewhat overlapped but are also very clearly broadened. Attributing this width to lifetime broadening yields the psec lifetimes listed in Table I for the ν′ = 7 and 8 levels. (The assignment of these lines to ν′ = 7 and 8 rests on the same principles that led to the other line assignments in this region, i.e., extrapolation of the well behaved lower members of the progression.)

Table I reveals the roughly six orders of magnitude difference in measured lifetimes for ν₃′ = 0 – 8. However, another factor makes this observation even more remarkable. As Fig. 4 shows, vibrational states within a few cm⁻¹ energy of the higher ν₃′ levels fragmenting in 10 ps remain stable and fluoresce for a few μsecs.

In Fig. 5, we plot the vibrational intervals G(v) vs (v+1/2) for both the fluorescing and non-fluorescing overtones of ν₃′. As Fig. 5 shows, the plot is nearly a straight line with no
perceptable deviation between the "bright" and "dark" levels. The fit to all the levels yields $\omega_e = 313.8(4) \text{ cm}^{-1}$ and $\omega_e x_e = 2.29(4) \text{ cm}^{-1}$. Using the standard formula relating the above parameters and the dissociation energy $D_e$, yields $D_e \approx 10750 \text{ cm}^{-1}$. Referring to Fig. 5, we see that our experiments sample the potential approximately one-quarter of the way to the dissociation limit.

4. Conclusions

We have obtained for the first time the spectrum of CF$_3$S, the heaviest member yet observed of the methoxy family of radicals. We have found that the $\tilde{A} ^2A_1 \leftrightarrow \tilde{X} ^2E$ electronic transition in CF$_3$S has extensive vibrational structure in its LIF spectrum. However, we have also shown that many of the $\tilde{A}$ state vibrational levels are unobservable in the LIF spectrum. These levels are "dark" because of a very mode-selective non-radiative process, which is probably predissociation to CF$_3$+S.

We have probed the "dark" levels of CF$_3$S with a novel adoption of FDS. In this experimental technique, the large pulse-to-pulse signal variations typically present in double resonance experiments are greatly diminished by use of a "double-beam" technique that utilizes a CCD camera for imaging. The technique should have wide applicability in other double resonance schemes, such as stimulated emission pumping. We believe that FDS has great potential for expanding our knowledge of many small to moderate sized free radicals as evidenced by our present experiment and a similar, recent one on vinoxy.34

We plan to use FDS to investigate other members of the methoxy family. For example, the CF$_3$O LIF excitation spectrum shows little vibrational structure, with all the observed $\tilde{A}$ state levels exhibiting a clear shortening of their lifetimes compared to the radiating $\tilde{A}$ state levels of the other members of the methoxy family. Both observations for CF$_3$O indicate a similar, but more extensive predissociation. Likewise, photofragmentation in the $\tilde{A}$ state of CH$_3$O has recently attracted considerable interest and we think that FDS can further clarify the excited state spectroscopy and dynamics. Finally, we believe that other free
radicals probably have many hitherto unknown "dark" states that are of great importance to their photochemistry and which can be productively probed by FDS.

5. Acknowledgment

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References


therein.


32. M. C. Yang, D. Powers, and T. A. Miller, to be published.


TABLE 1
Measured Lifetimes in $\mu$sec of the $\tilde{A} A_1$

state of CF$_3$S as a function of quanta in the $\nu'_3$ vibrational mode

<table>
<thead>
<tr>
<th>$\nu'_3$</th>
<th>$\tau^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.7</td>
</tr>
<tr>
<td>1</td>
<td>2.9</td>
</tr>
<tr>
<td>2</td>
<td>3.0</td>
</tr>
<tr>
<td>3</td>
<td>2.5</td>
</tr>
<tr>
<td>4</td>
<td>$38 \times 10^{-3}$</td>
</tr>
<tr>
<td>5</td>
<td>$0.30-20 \times 10^{-3}$</td>
</tr>
<tr>
<td>6</td>
<td>...$^b$</td>
</tr>
<tr>
<td>7</td>
<td>$13 \times 10^{-6}$</td>
</tr>
<tr>
<td>8</td>
<td>$7 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

$^a$ These errors in the reported $\tau$ values are approximately 15
$^b$ Unmeasurable – see text
Figure Captions

1. Schematic diagram showing the overall experimental apparatus used for the FDS experiments.

2. Schematic diagram showing the details of portions of the PL and DL beams and the free jet expansion. The spatially resolved image of the laser induced fluorescence from the jet is imaged on the CCD. An experimental image of the PL fluorescence on the CCD camera is shown on the upper left. The integrals of the two peaks are denoted as $I_1$ and $I_2$. In the upper right, the relative timing of the photolysis, depletion, and probe lasers as well as the gating of the CCD is illustrated. All times are approximate.

3. Broad frequency scan of the CH$_3$S LIF spectrum. The transitions forming progressions in the active modes are indicated. Although not marked, most of the remaining transitions have been assigned to combination bands. The indication below the trace above 27500 cm$^{-1}$ has been studied by FDS with the PL fixed on the $\nu'_3 = 3$ transition indicated by the arrow.

4. Selected portion of $\tilde{A}^2A_1 \leftrightarrow \tilde{A}^2E$ spectrum using the FDS technique (top) and LIF technique (bottom).

5. Plot of $G(v)$ vs $(v+1/2)$ for $\nu'_3$ mode of $\tilde{A}^2A_1 CF_3S$. 