AIP | The Journal of Chemical Physics

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Citation: The Journal of Chemical Physics **106**, 7479 (1997); doi: 10.1063/1.473753
View online: http://dx.doi.org/10.1063/1.473753
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/106/18?ver=pdfcov
Published by the AIP Publishing

The spectroscopy of hexafluorothioacetone, a blue gas

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(Received 16 January 1997; accepted 5 February 1997)

The vibrational and electronic spectra of hexafluorothioacetone, $(CF_3)_2CS$, a novel blue gas, have been studied. *Ab initio* calculations of the vibrational properties of CF_3COF, CF_3CSF, and $(CF_3)_2CO$ were used to establish the feasibility and effectiveness of using theoretical predictions in the analysis of the spectra of perfluorinated compounds. These predictions have allowed us to obtain revised interpretations of the spectra of trifluoroacetyl fluoride and trifluorothioacetyl fluoride that are consistent with both experiment and theory and have allowed us to confirm a previous theoretical and experimental study of the spectrum of hexafluoroacetone. Similar calculations on hexafluorothioacetone predicted a ground state of C_2 symmetry, with the CF_3 groups staggered in an antieclipsed configuration and a pattern of vibrational frequencies similar to that of hexafluoroacetone. The gas phase and argon matrix infrared spectra and the Raman spectrum of hexafluorothioacetone were analyzed with the aid of the *ab initio* predictions and 20 of the 24 fundamentals were assigned. The blue color of the compound originates from very weak T_1-S_0 (800–675 nm) and S_1-S_0 (725–400 nm) transitions in the visible due to the $n-\pi^*$ electron promotion. Promotion of an electron from the π to the π^* orbital gives rise to a very strong electronic transition in the 230–190 nm region of the ultraviolet. No emission was observed on laser excitation of hexafluorothioacetone in the visible. *© 1997 American Institute of Physics.* [S0021-9606(97)00918-5]

I. INTRODUCTION

Thiocarbonyl compounds have a variety of spectroscopically interesting properties: They are often colored compounds due to low-lying T_1-S_0 and $S_1-S_0(n-\pi^*)$ electronic absorption bands, they often fluoresce or phosphoresce from these low-lying states and, in a variety of cases, they also exhibit anomalous emission from the higher $S_2(\pi-\pi^*)$ state.[1–3] The anomalous emission is in violation of Kasha's rule,[4] which generalizes that emission or photochemistry occurs from the lowest excited state of a given multiplicity; violations of this rule have constituted important tests of the theory of radiationless transitions. As emphasized in previous work,[5] the thiones are often very different from their carbonyl cousins, and study of their properties can be rewarding.

Unfortunately, along with their brighter attributes, the thiones also have a darker side. They often have foul odors, are usually very reactive unless stabilized by bulky or very electronegative substituents and have a strong tendency to dimerize, trimerize, or polymerize, making them difficult to isolate and study. For example, the prototypical compound, thioformaldehyde, is a very reactive, transient species which can only be studied in flow systems or matrices and polymerizes rapidly into a variety of odious products. Despite these difficulties, thioformaldehyde has been very intensely studied by spectroscopists and we now know a great deal about the ground and excited electronic states.[6–13]

In recent years, we have reported studies of some of the smaller alkyl thiocarbonyl compounds including laser induced emission studies of thioacetaldehyde[14] and thioacetone[15] by pyrolysis jet spectroscopy. Both compounds are red colored liquids, unstable with respect to polymerization at room temperature, and both exhibit gas phase phosphorescence from the T_1 state. The infrared spectra of these compounds have not been studied because of their reactivity. However, perfluorination dramatically decreases the reactivity, so that we were able to study the gas phase infrared and Raman spectra of trifluorothioacetyl fluoride (TTAF), a stable yellow gas, many years ago.[16]

Perfluorinated thioacetone or hexafluorothioacetone (HFTA) was first reported in 1961 by Middleton *et al.*[17] as a deep blue liquid with a boiling point of 8 °C. It was found to be insensitive to water or oxygen but readily dimerized in the presence of trace amounts of base. At that time, the compound was prepared by the inconvenient reaction of bis(perfluoroisopropyl)mercury with refluxing sulfur, although pyrolysis of hexafluorothioacetone dimer was also shown to regenerate the monomer. Subsequent work[18] showed that the dimer was readily synthesized by the reaction of hexafluoropropene and sulfur in the presence of potassium fluoride. As the dimer is a stable, easily handled compound, it is a convenient precursor to the monomer through simple vacuum pyrolysis.

As part of our continuing investigations of thione spectroscopy, we were interested in hexafluorothioacetone both as a candidate for infrared and Raman work and as a potential probe of methyl rotation dynamics in the S_1 and T_1 excited states. The stability of the monomer and the likelihood of being able to do laser excitation studies in the visible made it an attractive subject for study. The fact that it is a blue gas meant that the T_1-S_0 and S_1-S_0 electronic transitions were even lower in energy than those of thioacetone. It also suggested that the S_2-S_1 energy gap would likely be

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very large, so that anomalous fluorescence or photodissociation from S_2 might occur. Although the laser studies have turned out to be unproductive, we have succeeded in a detailed analysis of the vibrational spectrum, aided by *ab initio* calculations, and we have surveyed the electronic absorption spectrum throughout the UV-visible.

II. EXPERIMENT

Hexafluorothioacetone (HFTA) was prepared by the vapor phase pyrolysis of 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane (HFTA dimer) in vacuum at a temperature of 700–725 °C. The dark blue gaseous product was collected and stored at liquid nitrogen temperatures. Preliminary infrared investigations showed that the major impurities in the sample were hexafluoroethane, silicon tetrafluoride, and carbon disulfide. The former two were almost completely removed by pumping on the sample while cooling it to −100 °C and monitoring the infrared spectrum. The HFTA sample was always contaminated by small amounts of CS_2 which proved very difficult to eliminate completely. HFTA dimer, a colorless liquid which freezes at 24 °C, was synthesized by the reaction of perfluoropropylene, sulfur, and potassium fluoride according to the procedure of Dyatkin *et al.*[18]

Gas phase mid-infrared spectra were recorded on a Bomem DA3-02 FTIR spectrometer equipped with a KBr beamsplitter and an MCT detector. Far-infrared spectra were recorded down to 100 cm^{-1} on the same instrument using a variety of Mylar beam splitters. All the infrared spectra were recorded in a 10 cm cell with either CsI or polyethylene windows, as HFTA was found to dimerize readily when in contact with metals so that many experiments involving multiple relection techniques, employing aluminum coated mirrors, and metal fittings, were not feasible.

Gas phase Raman spectra were obtained using a Spex 1403 double monochromator with a cooled RCA 31034 photomultiplier and photon counting detection system. The Raman scattered radiation, excited by 100–400 mW of 514.5 nm laser light, was collected by a conventional 2-lens optical system. The HFTA gas sample was contained in a 4 cm o.d. Pyrex tube at a pressure of 400 Torr and the laser focused in a single pass at the center of the tube. Depolarization ratios were measured with a simple Polaroid-polarization scrambler combination. No fluorescence background was observed, although the excitation laser wavelength coincided with the S_1-S_0 absorption band of HFTA (*vide infra*).

Infrared matrix isolation experiments were done using a closed-cycle helium refrigerated system (Cryosystems LTS-21) coupled to a high vacuum line maintained at 10^{-7} Torr. Matrices were deposited on a CsI window cooled to 14 K and infrared spectra recorded at 0.5 cm^{-1} resolution using the Bomem FTIR described above. HFTA dimer/Ar mixtures (1:1000) were prepared, stored, and deposited in an all glass and quartz vacuum line. After passing through a small leak, the gas mixtures were pyrolyzed in a dimpled quartz tube (12 in.×1 in. i.d.) electrically heated to 725 °C before being deposited at an angle of 45° to the cold window. Low-resolution infrared spectra were taken intermittently during the deposition and 0.5 cm^{-1} spectra were taken at the end of the deposition process.

UV-visible spectra of HFTA were taken with a Shimadzu UV-3101PC scanning spectrophotometer at a resolution of 0.5 nm with a digitization interval of 0.1 nm using a 10 cm quartz cell at pressures from 0.75 to 350 Torr.

III. *AB INITIO* CALCULATIONS

The vibrational analysis of the spectrum of hexafluorothioacetone is complicated by the large number of normal modes (24), the lack of an experimentally determined structure, the impossibility of isotopic substitutions on the fluorine atoms, and the low molecular symmetry (C_2). It was anticipated that the normal modes would have substantial contributions from more than one symmetry coordinate, so that transferring vibrational frequencies or force constants from much smaller molecules might be misleading. Our approach has been to use *ab initio* predictions of the molecular structure, vibrational frequencies, normal coordinates, infrared intensities, and Raman depolarization ratios to aid in the analysis. As a stringent test of these predictions, we initially calculated the vibrational properties of trifluoroacetyl fluoride (CF_3COF), trifluorothioacetyl fluoride (CF_3CSF), and hexafluoroacetone [$(CF_3)_2CO$], molecules whose spectra have been previously analyzed.

The *ab initio* molecular orbital calculations were performed with the GAUSSIAN 92 series of programs[19] using a 6-311G(d) basis. The geometries were initially optimized without constraints and later constrained to the nearest appropriate point group for further calculations; no imaginary frequencies were found for any of the reported structures. The harmonic vibrational frequencies and absolute intensities were calculated at their ground state optimized geometries using analytic second derivative methods and scaled by the recently recommended factor[20] of 0.9051 to predict the vibrational fundamentals. The *ab initio* force field and molecular structure were used as input for a normal coordinate analysis, using the program of Hedberg and Mills,[21] to provide insight into the form of the normal modes from the potential energy distribution (PED). The normal modes were also visualized using HyperChem.[22]

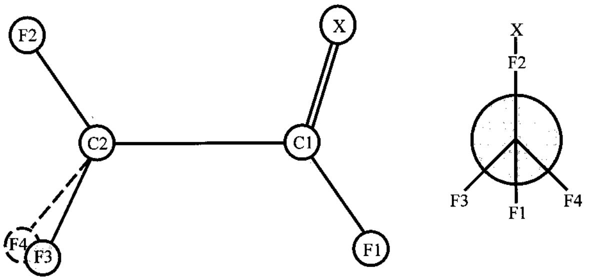

FIG. 1. Diagram showing the atomic numbering and C_s symmetry of CF_3CFO and CF_3CSF.

TABLE I. Geometry of trifluoroacetyl fluoride and trifluorothioacetyl fluoride.

Parameter[a]	CF_3CFO *Ab initio*	CF_3CFO Expt.[d]	CF_3CFS *Ab initio*
r(C1–X)	1.154	1.158±0.006	1.578
r(C1–C2)	1.529	1.525±0.006	1.526
r(C1–F1)	1.302	1.324±0.002	1.302
r(C2–F2)	1.300	1.324±0.002	1.301
r(C2–F3)[b]	1.310	1.324±0.002	1.311
θ(C2C1X)	125.9	129±2	127.8
θ(C2C1F1)	109.9	109.6±0.5	107.8
θ(C1C2F2)	110.3	109.6±0.5	112.2
θ(C1C2F3)[c]	109.7	109.6±0.5	109.3

[a] Bond lengths in Å, bond angles in degrees, see Fig. 1 for numbering of atoms.
[b] r(C2–F3)=r(C2–F4).
[c] θ(C1C2F3)=θ(C1C2F4).
[d] Reference 23.

A. Trifluoroacetyl fluoride (TAF)

Unconstrained geometry optimization of TAF gave a structure of C_s symmetry, as illustrated in Fig. 1. The oxygen, two carbons, and fluorines 1 and 2 lie in a plane such that F2 eclipses the oxygen atom. The optimized C_s structure is presented in Table I along with the electron diffraction structure obtained by Brake *et al.*[23] who found a single average C–F bond length of 1.324 Å and assumed local C_{3v} symmetry for the CF_3 group. Our results predict the C–F1 and C–F2 bond lengths to be about 1.300 Å, with slightly longer (1.310 Å) out-of-plane C–F3 and C–F4 bond lengths. The calculated C═O and C–C bond lengths and the various angles are in excellent accord with experiment. In previous theoretical work, Francisco and Williams[24] found that the C–F and C═O bond lengths were heavily dependent on the level of theory and not in good agreement with experiment, even at the MP2/6-31G(d) level and suggested that further experimental work may be necessary. We conclude that SCF calculations with a 6-311G(d) basis give a reasonable approximation to the molecular structure, given the limitations of the experimental geometry.

The predicted fundamental vibrational frequencies of TAF are collected in Table II. Under C_s symmetry, there are ten in-plane modes of a' symmetry and five out-of-plane modes of a'' symmetry; all are IR and Raman active. Examination of the form of the normal modes shows that substantial mixing of the symmetry coordinates occurs, particularly in the case of the CF_3 symmetric stretching and C–C stretching modes. This latter effect was noted previously by Tuazon *et al.*[25] who suggested that care must be exercised in making

TABLE II. Fundamental vibrational frequencies of trifluoroacetyl fluoride (in cm^{-1}).

Mode	Approximate description	*Ab initio*[a] (Int., depol. ratio)	Experiment[b] (Int., depol. ratio)	% diff.
a' species				
ν_1	CO str	1960 (308, 0.31)	1899 (108, 0.27)	3.2%
ν_2	CC str/CF_3 sym str	1377 (127, 0.60)	1340 (75, ⋯)	2.8%
ν_3	CF_3 asym str	1292 (394, 0.69)	1254 (180, ⋯)	3.0%
ν_4	CF1 str/CF_3 sym str	1122 (376, 0.72)	1099 (239, ⋯)	2.1%
ν_5	CF_3 sym str/CC str	814 (7, 0.04)	806 (33, 0.01)	1.0%
ν_6	CF_3 sym def/OCC def	697 (68, 0.74)	692[c] (109, 0.63)	0.7%
ν_7	CF_3 asym def	591 (2, 0.74)	595[c] (3.7, 0.78)	−0.7%
ν_8	OCC def/OCF1 def	427 (3, 0.71)	~426[c] (w, 0.72)	0.2%
ν_9	CC str/CF_3 sym def	381 (0.2, 0.44)	390 (2.5, 0.27)	−2.3%
ν_{10}	OCF1 def/CF_3 rock	226 (5, 0.73)	228 (4.1, ⋯)	−0.9%
a'' species				
ν_{11}	CF_3 asym str	1241 (348, 0.75)	1214 (192, ⋯)	2.2%
ν_{12}	OCF1 inversion	785 (31, 0.75)	761[c] (78, 0.15?)	3.2%
ν_{13}	CF_3 asym def	517 (14, 0.75)	519[c] (37, 0.70)	−0.4%
ν_{14}	CF_3 rock	242 (9, 0.75)	242 (m, 0.75)	0.0%
ν_{15}	torsion	49 (0.8, 0.75)	50 (0.25,⋯)	2.0%

[a] 6-311G(d,p) frequencies scaled by 0.9051; infrared intensities in km/mol; depol. ratio is the calculated Raman spectrum depolarization ratio.
[b] Experimental frequencies and depolarization ratios from Ref. 27; infrared intensities (10^{-3} cm^2/mol) from Ref. 26.
[c] Reassignment based on present work; see the text.

qualitative vibrational assignments in fluorine-containing compounds with C–F bonds adjacent to a C–C single bond, due to the extensive mixing of the C–F and C–C stretching coordinates.

The gas phase infrared spectrum of TAF was first studied by Loos and Lord,[26] who reported vibrational frequencies, intensities, band types, and assignments over the 35–3900 cm^{-1} range. Subsequently, Berney[27] obtained new infrared data along with liquid and solid phase Raman spectra including depolarization ratios for the stronger bands and reassigned some of the fundamentals. A few years later, Redington[28] analyzed matrix spectra of a variety of isotopically substituted trifluoroacetic acid species and proposed reassignments of the vibrational fundamentals of TAF to be consistent with those of similar CF_3-containing molecules.

Since the early experimental work, there have been three reported *ab initio* studies of the vibrational frequencies of TAF. Ottavianelli *et al.*[29] calculated the frequencies at the Hartree–Fock level with a 3-21G basis and found general agreement with the assignments of Berney. Pacansky *et al.*[30] explored the sensitivity of the vibrational frequencies of TAF and COF_2 to various levels of theory and concluded that scaled HF/6-31G* results gave excellent agreement with experiment, without recourse to larger basis sets or correlated wave functions. They did not advocate any changes in the assignments of Berney. In the most detailed study, Francisco and Williams[24] predicted the vibrational frequencies at the HF/3-21G and MP2/3-21G levels of theory and proposed a variety of reassignments.

Our assignments of the experimental data of Berney[27] are given in Table II. These are in general agreement with the proposals of Francisco and Williams[24] except for the values of ν_6 and ν_{12}. Berney assigned ν_6, the CF_3 symmetric deformation, to a medium intensity infrared band at 761 cm^{-1}, with a corresponding liquid phase Raman frequency of 770 cm^{-1} and a depolarization ratio of 0.15. This assignment is inconsistent with our *ab initio* prediction of a medium intensity band at 687 cm^{-1} (a frequency error of −10.8%) with a Raman depolarization ratio of 0.74. The stronger infrared band at 692 cm^{-1} with a depolarization ratio of 0.63 is readily reassigned as ν_6. The infrared band at 761 cm^{-1} may then be readily reassigned as ν_{12}, consistent with the *ab initio* frequency and intensity prediction. The only discrepancy is the measured Raman depolarization value of 0.15 for the feature at 770 cm^{-1}, which would have to be an a' fundamental. However, comparison of theory and experiment shows that a depolarization ratio of 0.15 is clearly anomalous for fundamentals of TAF in the 800–600 cm^{-1} region. The most likely explanation is that the Raman band at 758 cm^{-1} (depolarization ratio unfortunately not measured) corresponds to the IR fundamental at 761 cm^{-1} and that the Raman feature at 770 cm^{-1} is not a TAF fundamental.

The only other incongruity between the present assignments and those of Francisco and Williams[24] is in the descriptions of ν_2 and ν_3. At the HF/6-311G(d) level of theory, we find ν_2 to be a medium intensity band described as a mixture of CC stretching and CF_3 symmetric stretching motions and ν_3 to be a very intense band that is predominantly the CF_3 asymmetric stretch, entirely consistent with the infrared bands at 1340 and 1254 cm^{-1}, respectively. At the MP2/3-21G* level, the frequency of the intense CF_3 asymmetric stretch is predicted to be 17 cm^{-1} *above* the weaker CC stretching/CF_3 symmetric stretching mode, and on this basis Francisco and Williams reversed the assignments so that the band at 1340 cm^{-1}, although still ν_2, was attributed to the CF_3 asymmetric stretch. Experiment favors the HF/6-311G(d) interpretation, as the weaker band clearly occurs at higher frequency.

In summary, we conclude that the *ab initio* calculations give a reasonable geometry and reliable predictions of the scaled vibrational frequencies, relative infrared intensities and Raman depolarization ratios for trifluoroacetyl fluoride. The frequency scaling appears reliable for predicting the fundamentals to better than ±5% and the infrared intensities and Raman depolarization ratios have proven valuable in resolving discrepancies. A consistent interpretation of the available experimental data can be obtained on the basis of these predictions.

B. Trifluorothioacetyl fluoride (TTAF)

There have not been any previously reported *ab initio* studies of this molecule. Geometry optimization of trifluorothioacetyl fluoride gave a C_s symmetry structure very similar to that of trifluoroacetyl fluoride, as compared in Table I. Although the structure of TTAF has not been determined experimentally, the *ab initio* C=S bond length of 1.578 Å is comparable to that of $F_2C{=}S$ (1.589 Å)[31] and the similarity of the rest of the parameters to those of TAF suggest that the results are reasonable.

Our *ab initio* predictions of the vibrational parameters for TTAF are collected in Table III. Comparing the frequencies to those of TAF, we see that sulfur substitution lowers the C=X stretching frequency, allowing it to mix with the CC stretching mode, and diminishing the intensity of ν_1 in TTAF. The a'' and a' CF asymmetric stretching modes have similar frequencies in both molecules, but the other a' CF stretches differ substantially in both frequency and relative intensity. These differences can be traced to more pronounced mixing of the CC stretching coordinate with the CF stretching coordinates in TAF. Most of the low frequency modes are similar in the two molecules, although ν_{12} is calculated to be of medium intensity in TAF but very weak in TTAF.

We published the only experimental study of the vibrational spectrum of TTAF several years ago,[16] in which the assignments were made primarily by analogy to the TAF assignments of Berney.[27] As shown in Table III, most of the frequency assignments and infrared intensities are in good agreement with the present *ab initio* predictions. However, the calculations suggest that the weak bands at 398 and 505 cm^{-1} should be reassigned as ν_8 and ν_{13}, respectively. From these results, the 6-311G(d) basis set appears adequate for providing predictions of the vibrational frequencies, infrared intensities and Raman depolarization ratios of

TABLE III. Fundamental vibrational frequencies of trifluorothioacetyl fluoride (in cm^{-1}).

Mode	Approximate description	*Ab initio*[a] (Int., depol. ratio)	Experiment[b] (Int., depol.)	% diff.
a' species				
ν_1	CS str/CC str	1389 (83, 0.31)	1350 (m, p)	2.9%
ν_2	CF_3 asym str	1293 (103, 0.35)	1243 (s, ⋯)	4.0%
ν_3	CF1 str/CF_3 asym str	1270 (850, 0.47)	1227 (vs, ⋯)	4.6%
ν_4	CF_3 sym str/CF1 str	1061 (217, 0.58)	1049 (s, ⋯)	1.1%
ν_5	CF_3 sym str/sym def	765 (20, 0.06)	764 (m, p)	0.1%
ν_6	CF_3 asym def	581 (10, 0.66)	585 (w, ⋯)	−0.7%
ν_7	CS str/SCF1 def	546 (15, 0.21)	551 (m, p)	−0.9%
ν_8	SCF1 def/CF_3 rock	402 (1, 0.73)	398[c] (w, ⋯)	1.0%
ν_9	CC str/CF_3 rock	318 (0.3, 0.50)	328 (w, p)	−3.0%
ν_{10}	SCC def/SCF1 def	211 (2, 0.74)	221 (w, ⋯)	−4.5%
a'' species				
ν_{11}	CF_3 asym str	1230 (368, 0.75)	1183 (s, ⋯)	4.0%
ν_{12}	SCF1 inversion	685 (0.1, 0.75)	⋯	⋯
ν_{13}	CF_3 asym. def.	508 (6, 0.75)	505[c] (w, ⋯)	0.6%
ν_{14}	CF_3 rock	232 (3, 0.75)	228 (w, ⋯)	1.8%
ν_{15}	torsion	47 (0.03, 0.75)	<50	⋯

[a] 6-311G(*d*,*p*) frequencies scaled by 0.9051, infrared intensities in km/mol, depol. ratio is the calculated Raman spectrum depolarization ratio.

[b] Experimental frequencies, relative intensities, and depolarizations (p=polarized) from Ref. 16.

[c] Reassignment based on present work; see the text.

the sulfur analog of trifluoroacetyl fluoride. The scaled frequencies give predictions of the vibrational fundamentals reliable to about ±5%.

C. Hexafluoroacetone (HFA)

Geometry optimization of hexafluoroacetone gave a structure of C_2 symmetry as illustrated in Fig. 2 and Table IV. The carbon atom framework and the oxygen atom lie in a plane, with the CF_3 groups twisted slightly away from each other. Electron diffraction structures for HFA has been reported by Hilderbrandt *et al.*[32] and Boulet,[33] assuming local C_{3v} symmetry for the CF_3 groups. Our *ab initio* predictions, and earlier HF-SCF 3-21G results,[34] compare favorably to the Boulet[33] structure (Table IV), and less favorably to the Hilderbrandt *et al.*[32] geometry. In particular, the C═O bond length of 1.246±0.014 Å in the latter structure is very long compared to the 1.154 Å value in TAF.

The predicted vibrational frequencies of HFA are collected in Table V. As in the simpler molecules TAF and TTAF, the normal modes in HFA are often complicated, involving substantial contributions from more than one symmetry coordinate; our approximate descriptions refer to the dominant motions as given by the potential energy distribution. In previous work at the HF-SCF 3-21G level, Compton *et al.*[34] calculated the vibrational frequencies of HFA and used the force constants to do a normal coordinate analysis

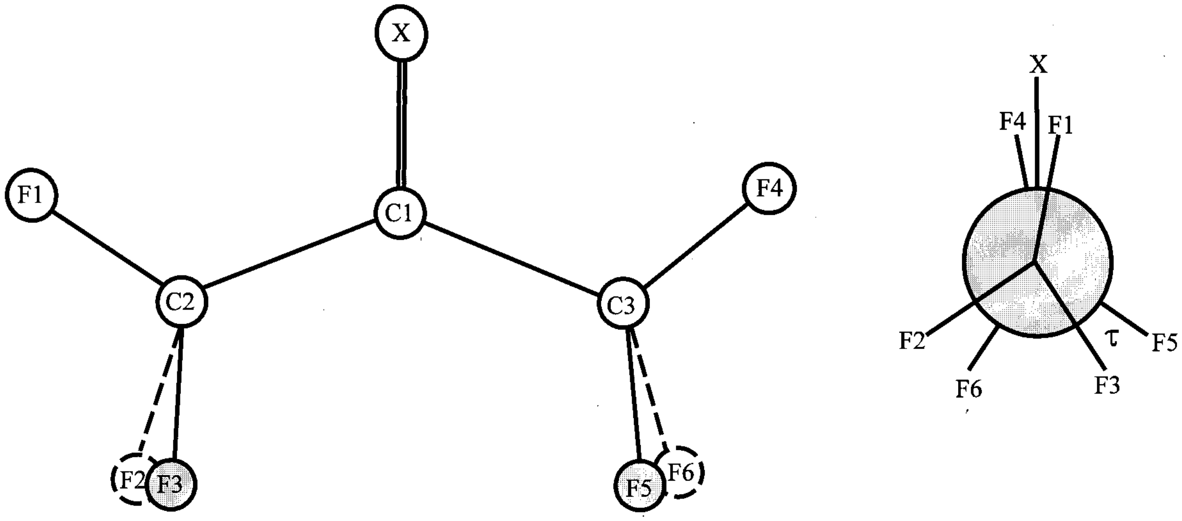

FIG. 2. Diagram showing the atomic numbering and C_2 symmetry of $(CF_3)_2C{=}O$ and $(CF_3)_2C{=}S$.

TABLE IV. Geometry of hexafluoracetone and hexafluorothioacetone.

Parameter[a]	$(CF_3)_2CO$ *Ab initio*	$(CF_3)_2CO$ Expt.[d]	$(CF_3)_2CS$ *Ab initio*
r(C–X)	1.168	1.185±0.020	1.582
r(C–C)	1.540	1.527±0.015	1.532
r(C–F1)[b]	1.301	1.321±0.007	1.303
r(C–F2)[b]	1.311	1.321±0.007	1.314
r(C–F3)[b]	1.312	1.321±0.007	1.313
θ(CCX)	121.4	120±4	122.9
θ(CCF1)[c]	110.2	110.3±1.0	112.0
θ(CCF2)[c]	109.6	110.3±1.0	109.8
θ(CCF3)[c]	110.6	110.3±1.0	110.5
τ	18.6	0	19.5

[a] Bond lengths in Å, bond angles in degrees, see Fig. 2 for orientation of atoms.

[b] r(C–F1) = r(C–F4); r(C–F2) = r(C–F5); r(C–F3) = r(C–F6).

[c] θ(CCF1) = θ(CCF4); θ(CCF2) = θ(CCF5); θ(CCF3) = θ(CCF6).

[d] Reference 33.

and obtain potential energy distributions for the various modes. Although their calculations predicted a C_2 structure, it was found that coordinates that transform according to different C_{2v} symmetry species do not couple appreciably in the C_2 structure, in agreement with molecular symmetry group[35] arguments that favor classifying the nontorsional modes under C_{2v} symmetry. This allows the modes to be classified as in-plane or out-of-plane, which is very useful in the analysis and in using visualization programs, as we have done, for describing the normal modes. Our results are in good accord with their predictions.

The infrared and Raman spectra of HFA were first analyzed by Birney[36] who concluded that the molecule had C_s symmetry, based on Raman polarization data. At almost the

TABLE V. Fundamental vibrational frequencies of hexafluoroacetone (in cm^{-1}).

Mode	Approximate description[a]	*Ab initio*[b] (Int., depol. ratio)	Experiment[c] (Int., depol.)	% diff.
a species				
ν_1	CO str	1906 (96, 0.38)	1806 (s, p)	5.5%
ν_2	CF_3 asym str(ip)	1313 (390, 0.67)	1341 (s, dp)	−2.1%
ν_3	CF_3 sym str/sym def	1268 (248, 0.68)	1254 (m, p)	1.1%
ν_4	CF_3 asym str(op)	1206 (2, 0.74)	1169 (vw, dp)	3.2%
ν_5	CF_3 sym str/sym def	775 (1, 0.00)	772 (m, p)	0.4%
ν_6	CF_3 asym def/rock(ip)	631 (0.9, 0.46)	631 (w, p)	0.0%
ν_7	CF_3 asym def(op)	538 (0.0, 0.75)	533 (m, dp)	0.9%
ν_8	CF_3 asym def(ip)/CC str	472 (10, 0.39)	466 (m, p)	1.3%
ν_9	CF_3 rock(ip)/CC str	316 (0.8, 0.34)	317 (w, p)	−0.3%
ν_{10}	CF_3 rock(op)	264 (0.2, 0.71)	264 (m, dp)	0.0%
ν_{11}	C–C–C bend	145 (1, 0.12)	⋯	⋯
ν_{12}	CF_3 torsion	46 (0.0, 0.75)	⋯	⋯
b species				
ν_{13}	CC str/CF_3 sym str	1375 (243, 0.75)	1341 (s, dp)	2.5%
ν_{14}	CF_3 asym str(op)	1264 (647, 0.75)	1274 (s, p)	−0.8%
ν_{15}	CF_3 asym str (ip)/(op)	1238 (75, 0.75)	1220 (vs, p)	1.5%
ν_{16}	CF_3 sym str/CO wag(ip)	971 (258, 0.75)	971 (s, ⋯)	0.0%
ν_{17}	CO wag(op)/CF_3 rock(op)	800 (14, 0.75)	800 (?, ⋯)	0.0%
ν_{18}	CF_3 sym def/str	717 (79, 0.75)	717 (s, ⋯)	0.0%
ν_{19}	CF_3 asym def(ip)	531 (14, 0.75)	530 (m, dp)	0.2%
ν_{20}	CF_3 asym def(op)	505 (14, 0.75)	508 (m, dp)	−0.6%
ν_{21}	CO wag(ip)/CC str	370 (0.7, 0.75)	368 (w, dp)	0.5%
ν_{22}	CF_3 rock(ip)	277 (6, 0.75)	273 (m, ⋯)	1.5%
ν_{23}	CF_3 rock(op)/CO wag(op)	195 (11, 0.75)	192 (m, dp)	1.6%
ν_{24}	CF_3 torsion	46 (0.4, 0.75)	⋯	⋯

[a] Approximate descriptions using the symmetry coordinates defined in Ref. 34. Asymmetric coordinates are labeled as ip or op to denote their symmetry with respect to the C–C–C plane.

[b] 6-311G(d) frequencies scaled by 0.9051, infrared intensities in km/mol, depol. ratio is the calculated Raman depolarization ratio.

[c] Experimental frequencies from Ref. 34, IR gas phase intensities from Ref. 36 and Raman depolarizations (p=polarized, dp=depolarized) from liquid phase data of Ref. 34.

TABLE VI. Fundamental vibrational frequencies of hexafluorothioacetone (in cm^{-1}).

Mode	Approximate description[a]	*Ab initio*[b] (Int., depol. ratio)	Experiment[c] (Int., depol.)	% diff.
a species				
ν_1	CS str/CC str	1381 (184, 0.34)	1324 (m, p)	4.3%
ν_2	CF_3 asym str(ip)	1296 (88, 0.24)	1262 (m, ⋯)	2.7%
ν_3	CF_3 asym str(op)	1199 (5, 0.60)	⋯	⋯
ν_4	CF_3 sym str/CS str	1167 (505, 0.49)	1159 (s, ⋯)	0.7%
ν_5	CF_3 sym str/sym def	762 (15, 0.03)	764 (w, p)	−0.03%
ν_6	CF_3 asym def(ip)	583 (0.5, 0.38)	580 (⋯, ⋯)	0.5%
ν_7	CF_3 asym def(op)	547 (0.0, 0.74)	550 (⋯, p)	−0.5%
ν_8	CF_3 rock(ip)/CC str/CS str	418 (7, 0.35)	417 (w, p)	0.2%
ν_9	CF_3 rock(ip)/CC str	332 (0.2, 0.18)	332 (vw, p)	0.0%
ν_{10}	CF_3 rock(op)	285 (0.8, 0.67)	286 (vw, ⋯)	−0.3%
ν_{11}	C−C−C bend	163 (0.7, 0.67)	159 (vw, ⋯)	2.5%
ν_{12}	CF_3 Torsion	57 (0.0, 0.74)	⋯	⋯
b species				
ν_{13}	CC str/CF_3 sym str	1316 (508, 0.75)	1296 (s, ⋯)	1.5%
ν_{14}	CF_3 asym str(op)	1253 (697, 0.75)	1202 (vs, ⋯)	4.2%
ν_{15}	CF_3 asym str(ip)	1217 (26, 0.75)	1174 (w, ⋯)	3.7%
ν_{16}	CF_3 sym str/CC str	937 (78, 0.75)	941 (m, ⋯)	−0.4%
ν_{17}	CS wag(op)/CF_3 rock(op)	729 (1, 0.75)	⋯	⋯
ν_{18}	CF_3 sym def	695 (54, 0.75)	696 (m, ⋯)	−0.1%
ν_{19}	CF_3 asym def(ip)	537 (9, 0.75)	539 (w, ⋯)	−0.4%
ν_{20}	CF_3 asym def(op)	501 (5, 0.75)	501 (w, ⋯)	0.0%
ν_{21}	CF_3 rock(ip)	309 (1, 0.75)	308 (vw, ⋯)	0.3%
ν_{22}	CS wag(ip)	239 (0.0, 0.75)	237 (vw, ⋯)	0.8%
ν_{23}	CS wag(op)	181 (1.5, 0.75)	175 (vw, dp)	3.4%
ν_{24}	CF_3 Torsion	40 (0.0, 0.75)	⋯	⋯

[a] Approximate descriptions using the symmetry coordinates defined in Ref. 34. Asymmetric coordinates are labeled as ip or op to denote their symmetry with respect to the C−C−C plane.

[b] 6-311G(*d*) frequencies scaled by 0.9051, infrared intensities in km/mol, depol. ratio is the calculated Raman depolarization ratio.

[c] Experimental frequencies, IR gas phase intensities and Raman depolarizations (p=polarized, dp=depolarized) from this work.

same time, Pace *et al.*[37] reported an analysis of the infrared spectrum assuming C_{2v} symmetry. Subsequently, Miller and Kiviat[38] remeasured the infrared and Raman spectra and reassigned a key vibration, negating the main reason for Berney's conclusion of C_s symmetry. In 1984, Compton *et al.*[34] further refined the Raman spectrum of HFA and used *ab initio* predictions of the vibrational frequencies to obtain a nearly complete assignment of all the fundamentals. These are given in Table V and are found to be in good agreement with our calculated frequencies, with no indications of misassignments. The only inconsistency is that the ν_1 fundamental is calculated to be 5.5% higher than the experimental value, a somewhat larger error than would be anticipated on the basis of the TAF and TTAF results.

D. Hexafluorothioacetone (HFTA)

There have not been any previously reported experimental or theoretical studies of the structure or vibrational frequencies of hexafluoroacetone. Our *ab initio* structure of HFTA (Table IV) is very similar to that of HFA except for the C=S bond length, which is within 0.004 Å of that calculated for TTAF. The CF_3 group torsional angles of HFA and HFTA are both small (~20°), suggesting that the vibrational modes of HFTA may also be classified using the in-plane and out-of-plane notation appropriate to the C_{2v} point group. The predicted vibrational frequencies and approximate descriptions of the normal modes, based on the dominant contributions to the potential energy distribution, are given in Table VI. Comparing the predicted frequencies of HFA and HFTA we find that most of the modes are analogous, with similar frequencies, PED's and relative intensities. Of course, the C=S stretch is lower than the C=O stretch and more heavily mixed with the C−C stretching coordinate, as was found for TTAF. The *a* symmetry CF_3 symmetric stretching mode is about 100 cm^{-1} lower in HFTA, as are the *b* symmetry in- and out-of-plane CS wagging modes. These considerations will be used in assigning the vibrational spectra of HFTA. Our studies of TAF, TTAF, and HFA suggest that the scaled vibrational frequencies should predict the fundamentals of HFTA to within ±5% and that the calculated infrared intensities and Raman depolarization ratios can be used as qualitative tools to aid in making assignments.

IV. SPECTROSCOPIC RESULTS AND ASSIGNMENTS

A. Vibrational spectra

The mid-infrared gas phase spectrum of hexafluorothioacetone is shown in Fig. 3. It consists of a set of very strong bands in the 1350–1150 cm^{-1} region, two weaker bands at

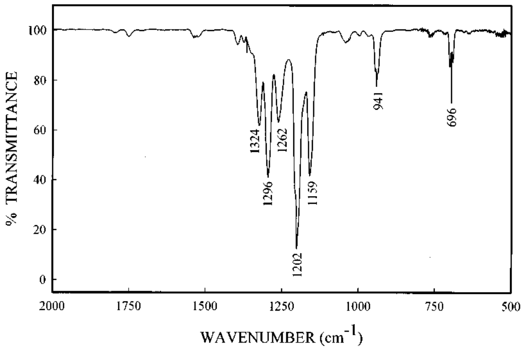

FIG. 3. Mid-infrared spectrum of 3.0 Torr of $(CF_3)_2C{=}S$ in a 10 cm cell at a resolution of 1.0 cm^{-1}.

941 and 696 cm^{-1} and a few very weak bands. As contamination by HFTA dimer was always a concern in these experiments, we show in Fig. 4 the gas phase spectrum of the dimer. Although there are strong features in similar regions in both spectra, the peak at 747 cm^{-1} in Fig. 4 is diagnostic for the presence of dimer and it was absent from all the gas phase HFTA spectra. The infrared spectrum of HFTA in an argon matrix, shown in Fig. 5, helped to untangle the overlapping bands in the 1350–1150 cm^{-1} region of the gas phase spectrum. Unfortunately, these spectra were unavoidably contaminated by dimer absorptions due to the presence of metal components in the matrix system. The gas phase Raman spectrum of HFTA is illustrated in Fig. 6. The strongest feature in the spectrum occurs at 696 cm^{-1}, coincident with one of the medium intensity bands in the infrared spectrum. As expected, the CF stretching modes (1300–1100 cm^{-1} region) are strong in the infrared spectrum but weak in the Raman spectrum. A compilation of all of the observed features in the infrared and Raman spectra is given in Table VII.

B. Vibrational assignments

1. C$=$S stretch

The C$=$S stretching mode is expected to occur in the same region and with approximately the same intensity as the C$=$S stretch in trifluorothioacetyl fluoride. This band should be between 1300 and 1350 cm^{-1} and would be of medium intensity in the infrared and a medium intensity polarized band in the Raman spectrum. The band at 1324 cm^{-1} is the obvious candidate for ν_1, with a calculated value of 1381 cm^{-1} and a frequency of 1350 cm^{-1} in TTAF. The drop in C$=$O frequency in going from TAF to HFA is paralleled in the sulfur compounds.

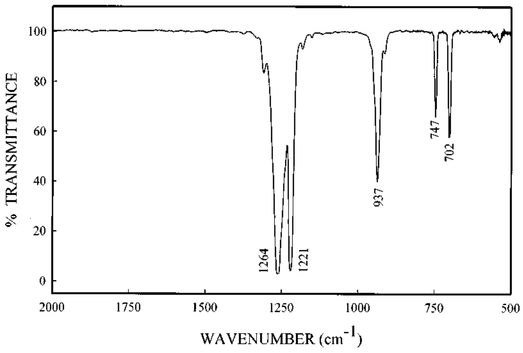

FIG. 4. Mid-infrared spectrum of 1.5 Torr of HFTA dimer in a 10 cm cell at a resolution of 1.0 cm^{-1}.

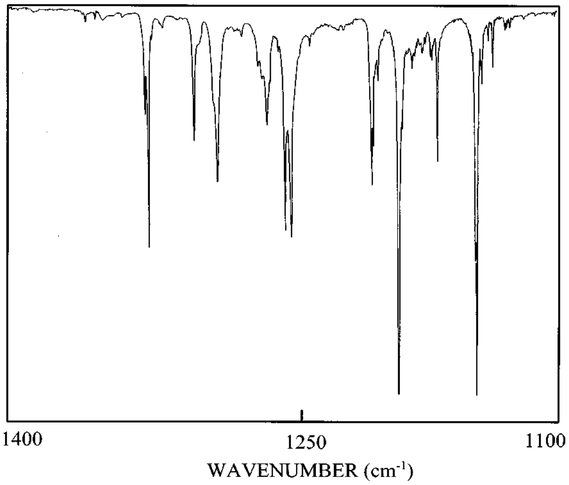

FIG. 5. Mid-infrared matrix isolation spectrum of hexafluorothioacetone at 14 K and a resolution of 0.5 cm^{-1}.

2. C–F stretches

The six C–F bonds in HFTA should give rise to six different, primarily C–F stretching modes in the 1350–1100 cm^{-1} region. The *ab initio* calculations predict that four of these will be strong infrared bands, along with the much weaker CF_3 asymmetric out-of-plane stretch of *a* symmetry and CF_3 asymmetric in-plane stretch of *b* symmetry. The gas phase infrared spectrum shows four strong ab-

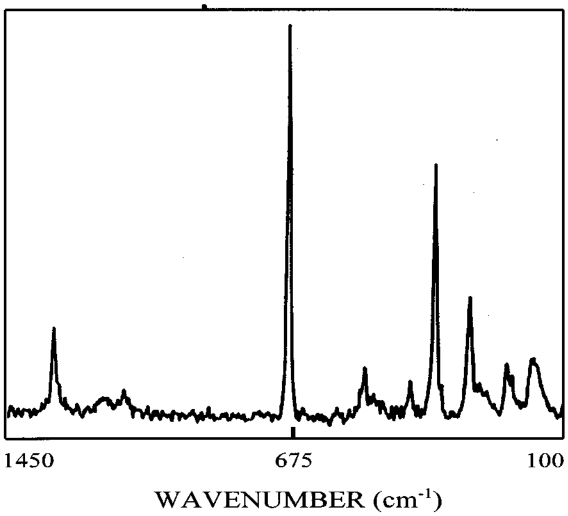

FIG. 6. Gas phase Raman spectrum of hexafluorothioacetone at a pressure of 340 Torr and a resolution of 10 cm^{-1}.

TABLE VII. Observed vibrational spectra of hexafluorothioacetone (in cm^{-1}).

IR (gas)		IR (matrix)[a]		Raman (gas)		
cm^{-1}	int.	cm^{-1}	int.	cm^{-1}	int.	Assignment
1324	m	1328	m	1324(p)	25	ν_1
		1304	m			?
1296	s	1293	m			ν_{13}
1262	m	1260	m			ν_2
1202	vs	1193	vs	1200	3	ν_{14}
		1174	w			ν_{15}
1159	s	1154	vs	1155	7	ν_4
1116	vw					C_2F_6
1030	vw	1023	vw			SiF_4
941	m	940	m			ν_{16}
764	w	763	vw	765(p)	100	ν_5
696	m	696	m			ν_{18}
639	vw					?
				580	17	ν_6
				550(p)	7	ν_7
539	w			530	shoulder	ν_{19}
				471(p)	10	dimer
501	vw					ν_{20}
417	w			417(p)	74	ν_8
397	vw					CS_2
389	vw					SiF_4
372	vw					
332	vw			334(p)	37	ν_9
308	vw			300	10	ν_{21}
286	vw					ν_{10}
				237	18	ν_{22}
220	vw					?
175	vw			175(dp)	22	ν_{23}
159	vw					ν_{11}

[a] Dimer absorption bands were also observed at 1268, 1256, 1216, 1212, 939, 934, 746, and 699 cm^{-1}.

sorption bands at 1296, 1262, 1202, and 1159 cm^{-1} which can be readily assigned as ν_{13}, ν_2, ν_{14}, and ν_4, respectively. The relative intensities and frequencies of these bands fall in the same order as the theoretical predictions, so the assignments are unambiguous. The infrared matrix spectrum shows a weak band at 1174 cm^{-1} which we assign as ν_{15}, since it is calculated to be about five times stronger than the weaker ν_3 band which remains unassigned. It is likely that ν_3 is coincident with ν_{15} or the much stronger ν_4 band at 1159 cm^{-1}. Our Raman spectra were too weak in this region to obtain reliable polarization data and only two bands at 1200 and 1155 cm^{-1} could be positively identified.

3. C–C stretches

Two nominally C–C stretching modes, ν_5 of *a* symmetry and ν_{16} of *b* symmetry, are expected to occur in the 900–700 cm^{-1} region. In HFA, the *a* mode is a medium intensity infrared band and the strongest Raman band in the spectrum, while the *b* mode is a strong infrared band and a weak[34] or missing[36] band in the Raman spectrum, consistent with our *ab initio* predictions for the IR intensities of ν_5 and ν_{16}. The C–C stretching mode of a' symmetry is also the most prominent Raman band in the spectra of TAF and TTAF. In the HFTA spectra, the higher frequency ν_{16} band occurs as a medium intensity infrared band at 941 cm^{-1} with no observed counterpart in the Raman spectrum and ν_5 shows up as a weak infrared band at 764 cm^{-1} and as a polarized, very intense Raman band at 765 cm^{-1}. The calculated PED shows that these modes actually involve very substantial contributions from the CF_3 symmetric stretches, as is often found for compounds with C–F bonds adjacent to carbon–carbon single bonds.[25]

4. C–F deformations

There should be six modes nominally describable as C–F deformations. Examination of the PED shows that these are the ν_6, ν_7 and possibly ν_8 *a* modes and the ν_{18} ν_{19} and ν_{20} *b* modes. Only ν_{18} is predicted to be a strong infrared band and it can readily be assigned to the feature at 696 cm^{-1}. The second most intense band in the Raman spectrum of HFA is ν_9 at 316 cm^{-1}, described as both CF_3 rock(ip) and C–C stretch. The corresponding mode in HFTA is ν_8, with a predicted frequency of 418 cm^{-1}, coinciding with the strong polarized Raman band at 417 cm^{-1}. The two other *b* symmetry modes are predicted to be weak infrared bands at 537 and 501 cm^{-1} corresponding to the observed features at 539 cm^{-1} (ν_{19}) and 501 cm^{-1} (ν_{20}). The ν_6 and ν_7 vibrations are calculated to give very weak infrared bands, which were not observed, but which could be assigned to Raman bands at 580 and 550 cm^{-1}, respectively. The other remaining fundamental in this region is ν_{17}, which involves a combination of CS out-of-plane wagging and

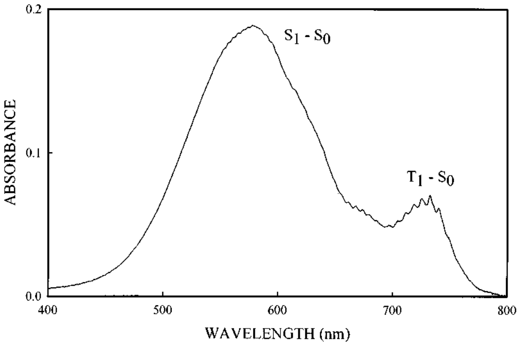

FIG. 7. Gas phase electronic absorption spectrum of hexafluorothioacetone in the visible recorded at a pressure of 350 Torr, pathlength of 10 cm and resolution of 0.5 nm.

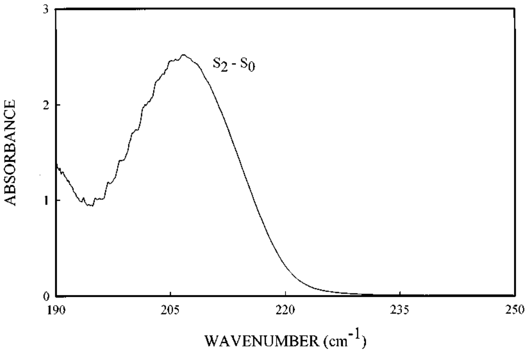

FIG. 8. Gas phase electronic absorption spectrum of hexafluorothioacetone in the ultraviolet recorded at a pressure of 0.8 Torr, pathlength of 10 cm and resolution of 0.5 nm.

CF_3 out-of-plane rocking; it is predicted to be a very weak band at 729 cm^{-1} and could not be found in the gas phase or matrix infrared spectra.

5. Low frequency modes

The remaining nontorsional modes involve CF_3 rocking, CS wagging and CCC skeletal bending motions. All of these modes are calculated to be very weak in the infrared and, by analogy with HFA data, are expected to have medium to weak intensities in the Raman spectrum. The ν_9 vibration, with a calculated frequency of 332 cm^{-1} and a similar PED to that of the strong Raman active ν_8 mode of HFA, shows up as a very weak IR band at 332 cm^{-1} with a strong polarized Raman line at 334 cm^{-1}. The CF_3 rocking modes ν_{10} and ν_{21}, with predicted frequencies of 285 and 309 cm^{-1} (264 and 273 cm^{-1} observed in HFA), are assigned to the infrared bands at 286 and 308 cm^{-1}. The CS wagging modes ν_{22} and ν_{23} are assigned to the Raman lines at 237 and 175 cm^{-1}; the former is absent in the infrared as predicted by the *ab initio* results. Finally, the CCC bending skeletal mode, ν_{11}, which is predicted to occur at 163 cm^{-1}, was tentatively identified as a weak shoulder on the side of the 175 cm^{-1} infrared band (ν_{23}).

6. Torsions

The *ab initio* calculations predict two torsional vibrations, both at 46 cm^{-1}, a frequency range beyond the capabilities of our instrumentation.

The results of the vibrational analysis are summarized in Table VII and the assigned fundamentals are compared to the *ab initio* predictions in Table VI.

C. Electronic spectra

As shown in Figs. 7 and 8, hexafluorothioacetone exhibits three electronic transitions in the UV-visible. The deep blue color of liquid HFTA at low temperatures is a result of the two overlapping band systems in the 800–400 nm region. By analogy with previous studies of the spectra of thiones,[1–3] these can be assigned as the $\tilde{a}\ {}^3A - \tilde{X}\ {}^1A$ (800–680 nm) and $\tilde{A}\ {}^1A - \tilde{X}\ {}^1A$ (680–400 nm) electronic transitions, which involve promotion of a nonbonding electron on the sulfur atom to the π antibonding orbital. Both transitions are expected to be weak, as the former is spin-forbidden and the latter is orbitally forbidden in molecules of C_{2v} or higher symmetry. The measured oscillator strengths of the two transitions are $f = 2.0 \times 10^{-6}$ for the $T_1 - S_0$ system and $f = 1.9 \times 10^{-5}$ for the $S_1 - S_0$ system, comparable to the values measured previously[16] for the analogous band systems of TTAF. The $T_1 - S_0$ transition shows some poorly resolved vibronic structure with an average interval of about 140 cm^{-1}. It is likely that these low frequency intervals correspond to activity in the excited state CS out-of-plane wagging mode, similar to that observed in the $T_1 - S_0$ spectra of CH_3CHS[14] and $(CH_3)_2CS$.[15] Attempts were made to observe laser induced emission from HFTA vapor excited throughout the visible absorption bands, in both static cells and using the pyrolysis jet technique,[39] but no signals were detected.

In the ultraviolet, HFTA has a strong electronic transition in the 230–190 nm region as shown in Fig. 8, with $\lambda_{\max} = 207$ nm and $\epsilon_{\max} = 6200\ \ell\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-1}$. The weak structure on the high energy side of this spectrum is due to the very strong ${}^1\Sigma_u^+ - {}^1\Sigma_g^+$ band system of CS_2 present as an impurity in the HFTA sample. The hexafluorothioacetone transition is assigned as the $S_2 - S_0$ ($\pi - \pi^*$) allowed electron promotion. Although Rydberg transitions have been observed in this region in the spectra of various thiones,[40,41] the breadth of this transition (4000 cm^{-1} FWHM) and measured oscillator strength of 0.11 are more consistent with a valence-shell electron promotion. Interference from strong CS_2 emission frustrated attempts to search for $S_2 - S_0$ emission in HFTA using laser induced fluorescence techniques.

V. DISCUSSION

In this work, we have explored the vibrational and electronic spectra of hexafluorothioacetone, a novel blue gas, for the first time. Although our initial goal of studying the electronic spectra by LIF techniques has been thwarted by mother nature, we have been able to obtain a rather complete analysis of the vibrational spectra and have surveyed the UV-visible absorption spectra.

It is clear from our *ab initio* calculations of the vibrational properties of TAF, TTAF, and HFA that the HF-SCF method with a 6-311G(d) basis, along with appropriate scaling factors, gives predictions of the vibrational fundamentals, relative infrared intensities and Raman depolarization ratios which are sufficiently reliable as to be useful in the assignment of spectra. These predictions have allowed us to finally obtain interpretations of the spectra of trifluoroacetyl fluoride and trifluorothioacetyl fluoride that are consistent with both experiment and theory. Our calculations also confirm the earlier experimental and *ab initio* attack on the spectrum of hexafluoroacetone by Compton *et al.*[34] in which 21 of the 24 vibrational fundamentals were observed and assigned. In the present work, we have succeeded in identifying 20 of the vibrational fundamentals of hexafluorothioacetone, with no significant discrepancies between theory and experiment. As anticipated, the vibrational spectra of HFA and HFTA are very similar, with very strong CF_3 and C═O or C═S stretching modes in the 1900–1100 cm^{-1} regions and much weaker bending, wagging, rocking, and torsional modes at lower energies. The calculated PEDs show that very few vibrations can be identified with a single symmetry coordinate in either molecule.

The UV-visible spectrum of HFTA exhibits three distinct transitions which are readily assignable based on previous studies of other thiones. The T_1-S_0 oscillator strengths of TTAF (1.9×10^{-6}),[16] HFTA (2.0×10^{-6}), H_2CS ($\sim4\times10^{-6}$),[42] and H_2CO (1.9×10^{-6})[43] are very similar. Although spin–orbit coupling is expected to be more efficient in the sulfur compounds, the larger energy gap between T_1 and the higher singlet states of the thiones mitigates against greater intensity borrowing relative to that of formaldehyde. In contrast, the S_1-S_0 oscillator strengths of TTAF (5.3×10^{-5}),[16] HFTA (1.9×10^{-5}), and H_2CS ($\sim4\times10^{-5}$)[42] are much smaller than that of formaldehyde (2.4×10^{-4}),[44] reflecting less efficient vibronic coupling to higher electronic states in the thiones.

The absence of HFTA emission on laser excitation indicates that the first excited singlet and triplet states decay nonradiatively, presumably by efficient internal conversion and/or intersystem crossing pathways. Whether the S_2 state emits is still unknown, due to the previously described experimental difficulties. Judging from the onset of each electronic transition, HFTA has a S_2-S_1 energy gap of about 29 700 cm^{-1}, more than double the S_1-S_0 separation of 13 800 cm^{-1}, so that fluorescence or photochemistry directly from the S_2 state, in violation of Kasha's rule,[4] is very probable. Whether S_2 emission can ever be observed depends, of course, on the competition between the fluorescence and the photodissociation decay pathways; at the onset of the S_2-S_0 absorption band (230 nm) it is likely that the latter predominates.

Further studies would be useful in clarifying various aspects of the spectroscopy of hexafluorothioacetone. The molecular structure could be determined by electron diffraction, which would help validate the *ab initio* predictions. The Raman spectrum and polarization data could be substantially improved with access to a brighter laser source and a multipass excitation system. The far-infrared spectrum could also be extended to lower wave numbers to observe the torsional fundamentals.

ACKNOWLEDGMENTS

The authors wish to thank Linda Osborne for recording the Raman spectra, Dr. J. Laboy and Jeff York for recording various matrix spectra and James Vollmer for his help with the *ab initio* calculations. Many useful discussions with Roger Grev are also gratefully acknowledged. Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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