Broadband Transient Infrared Laser Spectroscopy of Trifluorovinyl Radical, C₂F₃: **Experimental and ab Initio Results**

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The trifluorovinyl radical $(C_2F_3^{\bullet})$ is identified by using infrared spectroscopy. Real-time broadband infrared laser and diode infrared laser absorption spectra of the trifluorovinyl radical were measured. The radical was generated from UV laser photolysis of trifluoroiodoethene (C₂F₃I) at 248 nm in the gas phase. The observed vibrational frequencies and intensities $[\nu_2, 1290]$ (± 5) cm⁻¹, 106 (± 39) km mol⁻¹; and ν_3 , 1225 (± 5) cm⁻¹, 119 (± 41) km mol⁻¹] are in good agreement with ab initio values calculated in this work. Pseudo-first-order decay kinetics of the transient vibrational bands were observed. Analysis of the photoproducts with Fourier transform infrared spectroscopy showed that 1,3-hexafluorobutadiene (C4F6) was present in high concentration. It was probably formed from the reaction of trifluorovinyl radical with trifluoroiodoethene, as is consistent with the observed kinetics.

Introduction

The study of transient molecules was by his own admission, a unifying force behind the research interests of George C. Pimentel. He said, "A theme has run through my research literally since I was a graduate student. It has been to try to understand chemical bonding in molecules that do not have normal, satisfied valence situations-for example, CH₃, CH₂ or CH rather than methane. That theme has pervaded everything I have done.¹

The matrix isolation technique and the rapid-scan infrared spectrometer were two of the methods developed by him in his laboratories in order to learn about chemical bonding. In the present work, the rapid-scan infrared spectrometer, recently developed by Young and Pimentel,² has been used to carry out the first characterization of the trifluorovinyl radical (C_2F_3) in the gas phase.

The molecular structures of vinyl radicals, including trifluorovinyl, have been of interest for many years.³⁻⁶ Figure 1 shows the σ , π , and bridged structures that have been proposed for vinyl radicals at one-time or another. Electron spin resonance (ESR) experiments in liquid ethylene⁷ and matrices⁸⁻¹⁰ have demonstrated that the vinyl radical is a σ species. Kanamori et al. have used infrared diode laser kinetic spectroscopy to detect the c-type CH₂ wagging mode of the vinyl radical near 895 cm^{-1,11} They have found that the α -hydrogen tunnels between two equivalent σ vinyl structures. A σ -trifluorovinyl radical has been detected by Kasai¹² in an argon matrix using ESR. It was generated by the UV photolysis of C_2F_3I .

In this work we present chemical trapping evidence, transient infrared vibrational bands, transient kinetics, and ab initio results to identify and characterize the σ -trifluorovinyl radical.

Experimental Section

An excimer laser is used to photolyze trifluoroiodoethene, C₂F₃I, to give trifluorovinyl radical and iodine. The transient trifluorovinyl radical is then probed with a broadband infrared laser spectrometer or a high-resolution infrared diode laser spectrometer to acquire the rovibrational spectrum. The temporal behavior is acquired with the broadband system. Both the broadband infrared laser spectrometer^{2,13-15} and the high-resolution infrared diode laser spectrometer^{16,17} have been described in detail. Here, only a brief description will be presented along with changes to the spectrometers made specifically for these experiments.¹⁸

The gas-handling system is common to the broadband infrared laser spectrometer and the infrared diode laser spectrometer. The sample cell is made of Pyrex. It has a 2.54-cm inner diameter

and a 1-m zone of the precursor C_2F_3I and He for spectroscopy and kinetics. Extensions are fitted to the ends of the cell to purge the BaF_2 windows. A capacitance manometer is used to obtain pressure readings in the manifold, and flow meters are used to regulate the amount of gas flowing in the system.

The pump laser is an excimer laser operating on the KrF (248 nm) line. It is focused to a $2 \text{ mm} \times 3 \text{ mm}$ spot in the center of the cell with a 1-m cylindrical lens and turned by a 90° UV mirror. A special BaF_2 beam combining optic that has a dielectric coating is used to reflect the UV and transmit the IR probe beam. Two of these beam combiners are used. One combines the UV and IR light and the other separates them. The excimer was externally fired by the computer and a digital delay generator for the broadband infrared spectrometer. The excimer was externally fired by the combination of a boxcar and a signal generator for the diode laser spectrometer. The KrF line was typically run at 10 Hz, 250 mJ/pulse, and with a 30-ns fwhm pulse width.

Transients formed by photolysis with the excimer laser are probed with the IR laser. The broadband infrared light is generated by pumping a Cs atom heat pipe with an excimer-pumped broadband dye laser. An excimer laser (308 nm, 12-ns fwhm, 180 mJ/pulse) pumps a home-built broadband dye laser that uses an oscillator and amplifier configuration similar to that of Bethune.¹⁹ The dye laser energy was usually 12 mJ/pulse with a fwhm ot 8 ns. The output is peaked near 391 nm and has a 680-cm⁻¹ spectral bandwidth.

The broadband dye laser output is then down-coverted to generate IR laser radiation via the SERS process in a metal vapor

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Figure 1. Proposed σ , π , and bridged structures for the trifluorovinyl radical.

heat pipe, using the 6s-8s transition in atomic cesium. The IR pulse typically contained 5 μ J of total energy in the region 840-1340 cm⁻¹, with a pulse width of less than 1 ns. Separation of the residual dye laser light from the IR is accomplished with a Ge flat. The infrared light is collimated with a 0.75-m focal length gold mirror and focused with a 1.0-m focal length gold mirror, through a beam combiner, to a spot in the center of the gas cell where it overlaps with the photolysis beam. Here it acquires the signature of the transient absorber. After the IR passes through the sample cell it is recollimated with a 0.75-m gold mirror and sent into an adjoining room where it is focussed by a 7.5-cm focal length BaF₂ lens onto the 0.1-mm entrance slit of the monochromator.

The monochromator is used to disperse the broadband IR laser across a liquid nitrogen cooled mercury-cadmium-telluride (MCT) 1×120 element array. A 25 grooves/mm grating disperses approximately 2 cm⁻¹ on each detector element;²⁰ the total spectral coverage is then approximately 240 cm⁻¹. A 50 grooves/mm grating used in first order disperses approximately 1 cm⁻¹ per detector with total spectral coverage of approximately 120 cm⁻¹. In third order the 50 grooves/mm grating disperses approximately 30 cm⁻¹ across the array. The photoelectrons generated by the broadband IR laser are swept out to a low-noise preamplifier, integrator, and hold circuit. A multiplexer presents the analog signal voltage of each detector to an A/D interface card in the backplane of the computer, where it is digitized and subsequently stored.

The broadband spectrometer is calibrated with a reference gas such as methane.²¹ To obtain the reference spectrum, an empty cell background (I_0) is taken. The cell is filled with methane and buffer gas, and I is taken. The %T is obtained from the ratio I/I_0 . For the collection of transient spectra the spectrometer is used in the real-time-background (RTB) mode; first the excimer photolysis laser is fired, then the broadband IR probe laser is fired at a specific time delay, and I is acquired. Next, the photolysis excimer laser is disabled, and the broadband IR probe laser is fired, giving I_0 . I divided by I_0 is averaged until the desired S/N ratio is obtained, which usually requires 200-500 RTB cycles. This operating mode generates spectra so that the parent absorptions decrease when both lasers are fired (resulting in the condition defined as I), allowing for an increase in infrared photons to be dispersed across the appropriate detector elements. This allows for the absorption peaks of the parent and transient to be easily separated by noting the phase change of the signal. The absorbance units are defined by the usual relationship $A = \log (I_0/I)$. For this work a S/N of 1 corresponds to approximately 0.04 absorbance units.

The commercial infrared diode laser spectrometer used in this work was previously described in detail.^{16,17} Hence, only those details particular to the present experiment are given here. The commercial diode laser system consists of an evacuated cold head, a helium Displex, a cryogenic temperature stabilizer, and a laser control module. The cryogenic temperature stabilizer is simply a heater and temperature sensor to provide for temperature control. The laser control module regulates and ramps the diode laser



Figure 2. Gas-phase FTIR difference spectrum of a 4.58-Torr, 7.6-cm sample of C_2F_3I that has been photolyzed with a KrF excimer laser (20 shots, 420 mJ/pulse). The negative peaks are loss of C_2F_3I , and the positive peaks are photolysis products, identified as C_4F_6 .

current so that a spectrum can be acquired.

The infrared diode laser emission is coupled out of the cold head by a thallium bromoiodide window. It is collimated by a 19-mm focal length corner parabolic mirror and reflected into the sample cell by a series of gold-coated mirrors. The IR is then focused by a 1.5-m focal length mirror, reflected off another gold mirror, and transmitted through the UV/IR beam combiner. After passing through the sample cell, the beam is transmitted through the second UV/IR beam combiner. Next, the IR beam is collimated by a 75-cm focal length gold mirror, reflected back to the entrance slit of the monochromator by a set of gold mirrors, and focussed into the monochromator by a 19-mm focal length corner parabolic mirror. The monochromator is used to select a particular IR diode mode. After exiting the monochromator, the laser beam is collimated with a 20-cm focal length spherical mirror onto a MCT detector element.

The infrared signal from the detector is amplified and sent to two gated integrators and boxcar averagers. A reference of the IR intensity (I_0) is obtained by setting one boxcar gate at a time when the transient is not present, usually just before the photolysis laser is fired. The transient IR intensity signal (I) is acquired by placing the second boxcar gate at the specified time after the photolysis laser is fired. The reference and transient signals are subtracted in an analogue signal processor and then digitized and stored by the computer. The IR spectrum of the N₂O calibration gas²² was obtained by using frequency modulation techniques.

The iodotrifluoroethene (C_2F_3I) was obtained from PCR Inc.²³ It has a stated purity of 97–99%, as confirmed with an FTIR. The liquid is transferred to a glass bulb and put through several freeze-pump-thaw cycles before usage. The helium buffer gas was obtained from the University of California College of Chemistry Liquid Helium Facility and is 99.99+% pure.

Results

Photoproducts. The analysis of photoproducts resulting from UV photolysis provides indirect evidence that can help to identify a transient intermediate. For "static cell" experiments, a reference FTIR of a sample of C_2F_3I is obtained. After 30 shots at 420 mJ/pulse of the KrF photolysis laser are passed through the cell, another FTIR spectrum is taken. Figure 2 shows a difference spectrum obtained by subtracting the reference from the photolyzed sample. Before differencing, the spectra were originally ratioed to an empty cell and recorded in absorbance units. The negative peaks are loss of the precursor C_2F_3I , and the positive

⁽²⁰⁾ Each detector element consists of a 50 μ m by 50 μ m MCT pixel plus a 50- μ m space between pixels.

⁽²¹⁾ International Union of Pure and Applied Chemistry; Tables of Wavenumbers for the Calibration of Infra-Red Spectrometers; Crane, Russak & Company: Washington, DC, 1961.

⁽²²⁾ Guelachvili, G.; Rao, K. N. Handbook of Infrared Standards; Academic: Orlando, FL, 1986.

⁽²³⁾ PCR, Gainesville, FL 32602.



λ (μm)

Figure 3. Broadband (240 cm⁻¹) transient infrared spectrum obtained 700 ns after the UV photolysis (248 nm, 280 mJ/pulse) of a C_2F_3I/He (0.5/25.0 Torr). There were 200 RTB cycles. The spectrum is linear in wavelength. There is approximately 2 cm⁻¹ per detector element.



Figure 4. Broadband (120 cm⁻¹) transient infrared spectrum obtained 1 μ s after the photolysis of a C₂F₃I/He mixture at 248 nm. The C₂F₃I and He pressures are: 1.0 and 24.5 Torr. There were 200 infrared laser shots obtained after photolysis and 200 background infrared laser shots without photolysis. The spectrum is linear in wavelength. There is approximately 1 cm⁻¹ per detector element.

peaks correspond to photolysis products. It is suspected that 1,1,2,3,4,4-hexafluoro-1,3-butadiene (C_4F_6) would be a reasonable candidate for a photolysis product molecule, and its presence is evidenced by the spectra in Figure 2. Further studies found no evidence of secondary photolysis products.

Transient IR Bands. Given the capability of being able to conveniently search large spectral regions with the broadband infrared laser spectrometer, the location of transient bands can be found quickly; the procedure for doing this is demonstrated in the following figures. First we scan with the broadest spectral coverage available to look for evidence of a phototransient; Figure 3 depicts the broadband transient infrared spectrum in the region 1102-1343 cm⁻¹ taken 700 ns after the photolysis of the C_2F_3I . The upward excursions represent loss of C_2F_3I and the two large downward absorbances at 1291 and 1225 cm⁻¹ are the phototransient peaks. Next, we look at the phototransient peaks more closely and note that some structure is evident in Figure 4 (1191-1322 cm⁻¹, 1 μ s after the photolysis of C₂F₃I). Then each phototransient band can be dispersed across the array. Figure 5 shows a broadband transient infrared spectrum in the region 1206-1236 cm⁻¹ taken 975 ns after photolysis. Figure 6 contains a broadband transient infrared spectrum in the region 1270-1305 cm⁻¹ taken 2 µs after photolysis. Using the diode laser spectrometer, we obtained the highest resolution as shown in Figure 7 (1229.49-1230.02 cm⁻¹) and, with this capability, we are working toward a more complete understanding of this molecular system.



Figure 5. Broadband (30 cm⁻¹) transient infrared spectrum obtained for the 1225-cm⁻¹ band 975 ns after the photolysis of a C_2F_3I/He mixture at 248 nm. The C_2F_3I and He pressures are 1.0 and 100 Torr. There were 500 infrared laser shots obtained after photolysis and 500 background infrared laser shots without photolysis. The transient and background shots were collected alternatively. The spectrum is linear in wavelength. There is approximately 0.5 cm⁻¹ per detector element.



Figure 6. Broadband (30 cm⁻¹) transient infrared spectrum of the 1290-cm⁻¹ band obtained 2 ns after the photolysis of a C_2F_3I/He mixture at 248 nm. The C_2F_3I and He pressures are 1.0 and 101.0 Torr. There were 500 infrared laser shots obtained after photolysis and 500 background infrared laser shots without photolysis. The photolysis energy was 280 mJ per pulse. The spectrum is linear in wavelength.

Kinetics. The kinetic behavior of the transient bands also provides important clues to help determine the IR carrier. The natural logarithm of the absorbance for the peak at 1224.6 cm⁻¹ is given versus time and is depicted in Figure 8. This is one of our best decay cuves. A pseudo-first-order kinetic analysis, assuming the parent C_2F_3I is present in excess of the transient concentration, gives a straight line for the natural logarithm of the transient intensity versus time. The slope of the line for the log plots, calculated by a least-squares analysis,²⁴ is the effective rate constant, k_{eff} , for the reaction of the transient with excess of parent molecules in the cell. Division of this rate constant by the C_2F_3I pressure gives the rate constant normalized for each particular run. The rate constant for the two transient bands for several trials are given in Table I.

Within experimental error, the two bands (1290 and 1225 cm⁻¹) yield similar rate constants, identifying them to the same transient species. The pseudo-first-order kinetic analysis is also consistent with the radical-molecule reaction $C_2F_3' + C_2F_3I \rightarrow C_4F_6 + I$. A second-order plot consisting of $1/[C_2F_3^*]$ versus time shows

⁽²⁴⁾ Bevington, P. R. Data Reduction and Error Analysis for the Physical Sciences; McGraw-Hill: New York, 1969. Skoog, D. A., West, D. M. Principles of Instrumental Analysis; Saunders College: Philadelphia, 1980.



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Figure 7. Transient infrared spectrum of $C_2F_3^{\bullet}$ obtained with an infrared diode laser after the photolysis of a C_2F_3I/He mixture at 248 nm. The C_2F_3I and He pressures are 1.0 and 25.0 Torr. The noise scan was obtained with an empty sample cell. The calibration gas was N_2O .

TABLE I: Pseudo-First-Order Rate Constants for the Reaction of the Transient with the Parent Determined from Kinetics Plots for the Two Transient Bands

C ₂ F ₃ I/He, Torr	k_{1290} , ×10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹	$k_{1225}, \times 10^{-12}$ cm ³ molecule ⁻¹ s ⁻¹
0.5/25.0	8.6 (±4)	
0.5/25.0		8.7 (±4)
1.0/24.5	4.4 (±2)	• •
1.0/24.5		3.9 (±2)
0.5/49.5		4.6 (±2)
0.5/99.5		7.4 (±2)
0.5/199.5		5.0 (±2)

that the second-order radical-radical reaction is dominated by a first-order reaction mechanism under these experimental conditions. There was no noticeable pressure dependence of the reaction when a large pressure of helium is used.

Vibrational Band Intensities. The integrated vibrational band intensity for each transient vibrational band is directly calculated from the broadband infrared spectrum. Following the compilations of Rao and co-workers,²⁵ the vibrational band intensity is

$$S_{\nu}^{0} = \int_{-\infty}^{\infty} \left(\frac{1}{nl} \ln \frac{I_{0}}{I(\nu)} \right) d\nu \qquad (1)$$

where I_0 is the unattenuated intensity of the source radiation and $I(\nu)$ is the radiation actually detected at the frequency ν , n is the concentration of the transient, and I is the path length. In this work the integral in eq 1 is approximated by

$$S_{\nu}^{0} \approx A \Delta \nu / nl \tag{2}$$

where A is the peak absorbance and $\Delta \nu$ is the full width at half-maximum (fwhm). Figure 3 shows the transient infrared spectrum of the proposed trifluorovinyl radical 700 ns after the photolysis of C₂F₃I. The peak absorbances from Figure 3 are A₁₂₉₀ = 0.16 (±0.05) and A₁₂₂₅ = 0.18 (±0.05). Using an asymmetric rotor computer program combined with reasonable values for the rotational constants of C₂F₃[•] (see ab initio section), we predict a dense rovibrational spectrum. Direct comparison of the cal-



Figure 8. Natural logarithm of the peak intensity for the $C_2F_3^{\circ}$ transient band at 1224.6 cm⁻¹. The overall broadband scan was from 1206 to 1236 cm⁻¹. The C_2F_3I/He pressures were 0.5/49.5 Torr. Points collected before 700 ns are not used in the analysis.

culated vs measured spectra proved to be very difficult when considering the effects of pressure broadening as well as the dimensions of the detector. Both of these add in the smoothing out of the vibrational band contours to those measured with the broadband IR spectrometer. The uncertainty in the absorbance measurement results from the determination of the baseline and the finite signal-to-noise ratio of the scan. The frequency bandwidths and uncertainties are $\Delta v_{1290} = 34$ (± 2) and $\Delta v_{1225} = 34$ (± 2), with the uncertainty derived from the spacing between detectors in the array. The path length in the cell is l = 100 (± 5) cm; the presence of buffer gas used to purge the cell windows to reduce photolysis product buildup causes the relatively large uncertainty in the cell length.

The concentration of the trifluorovinyl radical in the photolysis cell is necessary to obtain an integrated band intensity. The following represent the assumed and, where applicable, the measured values for each contribution to n. The concentration of the precursor C_2F_3I in the cell was adjusted to a partial pressure of 0.50 (± 0.05) Torr, with the uncertainty attributable to the flow controllers and capacitance manometer. The ultraviolet absorption coefficient of C_2F_3I at 248 nm was measured on a commercial UV-visible absorption spectrometer to be 0.0058 (± 0.0005) Torr⁻¹ cm⁻¹, and the quantum yield formation of $C_2F_3^{\bullet}(\phi_{C_2F_3^{\bullet}})$ has been set equal to unity. This value is reasonable, since fluorinated alkyl iodides are known to have quantum yields near unity for C-I dissociation in this wavelength region. This has been shown for CF_3I at 248 nm and C_3F_7I at 266 nm.²⁶ Finally, the photolysis pulse energy was set at a value of 280 mJ, and the beam filled a volume of the cell equalling 29 (± 5) cm³ over the path length defined above. With these values, the radical concentration is calculated to be 3.1 (± 0.06) × 10¹⁵ C₂F₃*/cm³.

 S_{ν}^{0} divided by the quantum yield for formation of $C_2F_3^{\circ}$ from the photolysis of C_2F_3I at 248 nm is calculated for each vibrational band, and the values are

$$S_{*}^{0}(1290 \text{ cm}^{-1})/\phi_{C_{*}F_{*}*} = 106 \ (\pm 39) \text{ km mol}^{-1}$$
 (3)

$$S_{\nu}^{0}(1225 \text{ cm}^{-1})/\phi_{C,F,*} = 119 (\pm 41) \text{ km mol}^{-1}$$
 (4)

Ab Initio Results

The first reported calculation for trifluorovinyl radical used the INDO (intermediate neglect of differential overlap) method;²⁷ the only other published work is a more recent INDO calculation that has been done to assign the ESR spectrum of trifluorovinyl radical.¹² The ab initio calculations reported here were performed

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⁽²⁶⁾ Van Veen, G. N. A.; Baller, T.; De Vries, A. E.; Shapiro, M. Chem. Phys. 1985, 93, 277.

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TABLE II: UHF/6-31G* ab Initio Geometries for Trifluorovinyl Radical

· · · · · · · · · · · · · · · · · · ·	UHF/3-21G*	UHF/6-31G*	_
	C, Symmetry		_
r(C=C)	1.315	1.319	
$r(CF_{r})$	1.332	1.301	
$r(CF_{e})$	1.334	1.303	
r(CF_)	1.336	1.304	
∠(F CC)	128.67	126.56	
∠(F _e CC)	122.30	122.86	
∠(F _γ CC)	125.49	124.76	
	C_{2n} Symmetry		
r(C=C)		1.276	
r(CF _a)		1.281	
r(CF.)		1.315	
$\angle(\mathbf{F}_{\alpha}\mathbf{C}\mathbf{F}_{\beta})$		125.44	

TABLE III: UHF/6-31G* ab Initio Harmonic Frequencies and Intensities for the Normal Modes of Trifluorovinyl Radical

mode	freq, cm ⁻¹	scaled freq, ³¹ cm ⁻¹	IR int, km mol ⁻¹
$\nu_1(a')$	1863	1658	33
$\nu_2(a')$	1475	1313	251
$\nu_3(a')$	1348	1200	351
$\nu_4(a')$	968	862	28
$\nu_5(a')$	659	587	3
$\nu_6(a')$	514	457	3
$\nu_7(a')$	228	203	6
ν ₈ (a'')	464	413	7
v9(a'')	312	278	2

using the GAUSSIAN 86²⁸ package on the Berkeley Cray XMP.

The calculations were carried out at the UHF/3-21G* and UHF/6-31G* levels of theory. A planar structure for the radical was assumed. The energy of the optimized C_s 6-31G^{*} structure is -373.91954 hartrees. This corresponds to the σ radical in Figure 1. The force field analysis shows this structure to be a minimum. The equilibrium geometry is given in Table II. At the equilibrium geometry, the expectation value of S^2 is 0.97 (a pure doublet has $\langle S^2 \rangle = 0.75$, suggesting some spin contamination in the wave function. The rotational constants (in cm⁻¹) derived from the 6-31G* calculation are $A_e = 0.384$, $B_e = 0.129$, $C_e = 0.096$. This yields a Wang asymmetry parameter (κ) of -0.78, indicating that trifluorovinyl radical is an asymmetric rotor.29

The energy for the optimized $C_{2\nu}$ (π radical) structure is 7913 cm⁻¹ above the C_s structure, and the geometry for C_{2v} symmetry is also given in Table II. This structure is a saddle point on the potential energy surface. The expectation value of S^2 is 0.86 at the optimal C_{2v} geometry.

The ab initio harmonic vibrational frequencies and the inten-sities are given in Table III. The intensities are calculated in the double harmonic approximation.³⁰ The mass scaled normal modes are shown in Figure 9.

Discussion

Kasai used electron spin resonance to detect a σ -trifluorovinyl radical in an argon matrix.¹² He photolyzed C₂F₃I via the n \rightarrow σ^* transition, with a Xe lamp and Corning 7-54 UV filter to produce $C_2F_3^*$. We access the same $n \rightarrow \sigma^*$ transition of C_2F_3I by using a KrF excimer laser to produce $C_2F_3^*$ in the gas phase. A major photoproduct from the UV photolysis is C_4F_6 . Analysis of the time-resolved infrared decay of the two transient vibrational



Figure 9. UHF/6-31G* ab initio normal modes of trifluorovinyl radical.

TABLE IV: Comparison of the Vibrational Frequencies for the Asymmetric CF₂ Stretch and the Combination Symmetric CF₂ and CF Stretches for Molecules of the Structure C_2F_3X , Where X = Electron, H, D, F, Cl, Br, and I^a

molecule	asym CF_2 str, cm ⁻¹	sym CF_2 + CF_{α} str, cm ⁻¹	
 C ₂ F ₃ • ^{35a}	1290	1225	
C_2F_3 , ab initio ^{35b}	1313	1200	
$C_2F_3H^{35c}$	1362	1264	
$C_2F_3D^{35c}$	1323	1200	
C ₂ F ₃ F ^{35d}	1340	1186	
C ₂ F ₃ Cl ^{35d}	1336	1215	
$C_2F_3Br^{35d}$	1330	1203	
$C_2F_3I^{35e}$	1310	1172	

"The two normal modes are presented in Figure 10 for C_2F_3 " and C₂F₃Cl. All values are experimental unless otherwise noted.

bands proposed for $C_2F_3^*$ using pseudo-first-order kinetics indicates that C_4F_6 is formed by the reaction of C_2F_3I and C_2F_3 .

The ab initio results of the preceding section may now be compared with the experimental observations. Our experiment does not provide sufficiently detailed information to determine the rotational constants for $C_2F_3^*$, but good agreement of ab initio geometries with experimental geometries for CF containing molecules such as CF, CF₂, and fluorinated ethenes and methanes has been found elsewhere, and the results will be presented here.¹⁸ For CF bond lengths, the comparison of the known zero point structures with the theoretical equilibrium structures indicates that the 3-21G* calculated bond lengths are longer than experiment, and the 6-31G* calculated bond lengths are shorter than experiment; so we expect the CF bond lengths for $C_2F_3^*$ to be between the 3-21G* and 6-31G* values. The ab initio carboncarbon double bond lengths are consistently shorter than observations, with the 6-31G* values being closer to the experimental values. The agreement between theory and experiment for the bond angles is within $2-3^{\circ}$.

An HF/6-31G* calculation provides reasonable vibrational frequencies when scaled by a factor of 0.89.32 The mean absolute error at the HF/6-31G* level of theory between the scaled ab initio and observed vibrational frequency has been reported at 49 cm⁻¹ based on 165 frequencies for first-row molecules.³³ The scaled vibrational frequencies given in Table III for ν_2 (1313 cm⁻¹) and ν_3 (1200 cm⁻¹) are close to the two measured bands (1290 and 1225 cm⁻¹). The difference between the scaled ab initio

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Figure 10. Comparison of the normal modes, v_2 and v_3 , for $C_2F_3^*$ and $C_2F_3Cl.^{35}$ The experimental frequencies are listed.

UHF/6-31G* frequency for trifluorovinyl radical and the proposed experimental values is (-)23 cm⁻¹ for ν_2 and (+)25 cm⁻¹ for ν_3 . This agreement allows us to assign the experimental bands as follows: $v_2 = 1290 \ (\pm 5) \ \text{cm}^{-1} \ \text{and} \ v_3 = 1225 \ (\pm 5) \ \text{cm}^{-1}$. The ab initio calculation provides one more vibrational frequency, viz., v_4 at 862 cm⁻¹, in the operating range of the time-resolved infrared spectrometer, but apparently the limited experimental sensitivity precludes detection, since the band is predicted to be considerably weaker.34

Figure 10 contains a comparison of the two normal modes, the asymmetric CF₂ stretch and the symmetric CF₂ + CF_{α} stretch for C_2F_3 and C_2F_3Cl . This shows that there may be a consistent pattern for comparing the vibrational frequencies for molecules of the type C_2F_3X , where X = electron, H, D, F, Cl, Br, and I, since the normal modes appear to be similar. Table IV investigates this concept further; for each molecule, the asymmetric CF_2 stretch is higher in frequency, averaging 1334 cm⁻¹, than the symmetric $CF_2 + CF_{\alpha}$ stretch, averaging 1207 cm⁻¹.

A comparison of the experimental and ab initio integrated vibrational band intensities (S_r^0) further supports the contention that the trifluorovinyl radical is the transient captured in the broadband nanosecond infrared scans described here. Schaefer's group determined the vibrational frequencies and intensities for a series of 13 test molecules and radicals.³⁶ The analytic determination of dipole moment derivatives with respect to nuclear coordinates for closed-shell, open-shell unrestricted, and open-shell restricted Hartree-Fock wave functions was obtained with a wide

TABLE V: Comparison Theory with Experiments for the Integrated Vibrational Band Intensities for C₂F₃, $\phi_{C_2F_3}$. Set Equal to Unity

	S_{ν}^{0} , km mol ⁻¹	
C ₂ F ₃ [•] mode	expt	ab initio 6-31G*
$\nu_2(a')$ CF ₂ asym str	106 ± 39	251
$\nu_3(a')$ CF ₂ sym + CF _a str	119 ± 41	351
$\nu_4(a')$ frame breathing	<40	29

variety of basis sets. They found that "theory at the HF/6-31G(d)or higher levels correctly predicts the qualitative features of the infrared spectrum: the order and approximate ratio of intensities of the fundamentals. Hence this theory can be a useful tool in the identification of transient species"

The ab initio values for $S^0_{\mu}(\nu_2,\nu_3,\nu_4)$ and the experimental values for $S^0_{\mu}(\nu_2,\nu_3,\nu_4)/\phi_{C_2F_3}$, for $C_2F_3^*$ are given in Table V. Within experimental error the qualitative agreement between theory and experiment is evident; $S_{\nu}^{0}(\nu_{3}) \geq S_{\nu}^{0}(\nu_{2}) \geq S_{\nu}^{0}(\nu_{4})$.

We have found two phototransient IR bands between 1200 and 1300 cm⁻¹. Other transient molecules that one might expect to result from UV photolysis of C₂F₃I provide only one unknown vibrational band near the two transient bands found in this study. The α, α elimination of IF gives difluorovinylidene, F₂C==C:. A recent high level ab initio study of difluorovinylidene calculates one frequency in this region; the C-F asymmetric stretch was found to be at 1326 cm^{-1} with a vibrational band intensity at 302 km mol^{-1,37} Gallo and Schaefer suggest that the experimental value will be near 1260 cm⁻¹. The α,β elimination of IF would give difluoroacetylene, FC=CF. A recent matrix isolation study of difluoroacetylene³⁸ observed one band at 1341 cm⁻¹, which corresponds with the only predicted fundamental with significant vibrational band intensity, the C-F asymmetric stretch at 1377 cm⁻¹ with an intensity of 309 km mol⁻¹.³⁹ The α, α or α, β elimination of F₂ is energetically forbidden. The vibrational frequencies of other possible carbon-fluorine transients such as CF2⁴⁰ and CF⁴¹ have different experimentally determined frequencies from the two transient bands observed. The symmetric stretch of CF_2 is at 1225.0793 cm⁻¹, but this molecule can be dismissed because its rovibrational spectrum is significantly different from the one we observed.

Conclusion

The gas-phase time-resolved infrared vibrational frequencies and band intensities, $v_2 = 1290 \ (\pm 5) \ \text{cm}^{-1} \ 106 \ (\pm 39) \ \text{km mol}^{-1}$, and $\nu_3 = 1225 (\pm 5) \text{ cm}^{-1}$, 119 (±41) km mol⁻¹, obtained in this study, along with photoproduct analysis and kinetic and ab initio studies are thus consistent with the identification of the carrier as the σ -trifluorovinyl radical.

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