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IR and UV Absorption Spectrum of the Trifluoromethoxy Radical, $CF_3O\cdot$, Isolated in Rare Gas Matrices

Gustavo A. Argüello[†] **and Helge Willner***

FB 6-Anorganische Chemie, Gerhard-Mercator-Universität Duisburg, Lotharstrasse 1,
D-47048 Duisburg, Germany

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The trifluoromethoxy radical is prepared in high yields by vacuum flash pyrolysis of $CF_3OC(O)OOC(O)OCF_3$ or $CF_3OC(O)OOCF_3$ highly diluted in inert gases, and subsequently isolated in inert gas matrices by quenching the product mixture at low temperatures. In the IR spectrum, six fundamentals have been observed and C_s symmetry is concluded for the matrix-isolated $CF_3O\cdot$ radical by comparison with predicted band positions and band intensities from ab initio calculations. This finding is at variance with results from the analysis of the rotational resolved fluorescence excitation spectra and dispersed fluorescence spectra of gaseous $CF_3O\cdot$ radicals, where C_{3v} symmetry was found. Possible explanations for this discrepancy are given. The UV spectrum in the spectral region 28000−43000 cm^{-1} has been measured for the first time, and two different electronic transitions are observed. The structure of the low energy transition $\tilde{A}^2A_1 \leftarrow \tilde{X}^2E$ is in agreement with that in previous laser induced fluorescence spectra. Four vibrational progressions are found in the spectral range between the band origin at 28517 cm^{-1} and up to 32400 cm^{-1}. The spectroscopic results are compared with the gas phase and ab initio computed values and are discussed in detail.

Introduction

Fluorinated oxy and peroxy radicals are important intermediates in the atmospheric degradation of hydrofluorocarbons,[1−3] which are increasingly being used as chlorofluorocarbon replacements. All recent kinetic studies of the reactions between ozone and fluorinated radicals of the type $R_FO_x\cdot$ ($x = 0, 1, 2$) have shown that they have only a minor impact on the concentration of stratospheric ozone.[3−7] However, the simplest oxy and peroxy radicals containing only a single carbon atom, $CF_3O_x\cdot$ and $FC(O)O_x\cdot$ ($x = 1, 2$) are attracting increasing interest on account of their spectroscopic, structural, and chemical properties. Recent publications on $CF_3O\cdot$,[8−10] $CF_3OO\cdot$,[11] $FCO_2\cdot$,[12,13] and $FC(O)O_2\cdot$ [11] serve as examples. The most extensively investigated among these radicals is the trifluoromethoxy radical, $CF_3O\cdot$, which has been the subject of experimental and theoretical studies.

$CF_3O\cdot$ was first identified by a single IR absorption at 1223 cm^{-1} in 1985 by Andrews et al.[14] in a photochemical reaction between matrix-isolated CF_3I and O_3. The assignment of this band was supported by the predicted IR spectrum, reported in a theoretical study of $CF_3O\cdot$ by Francisco and Williams in 1984.[15] Later the IR band was also observed in another matrix isolation experiment,[16] but until now no further IR absorptions due to $CF_3O\cdot$ have been reported. As an additional consequence of the early theoretical study,[15] several laser-induced fluorescence[8,9,17,18] and dispersed fluorescence[10,17,18] spectra of $CF_3O\cdot$ radicals have been recorded in the gas phase. From the analyses of laser-induced fluorescence excitation spectra of jet-cooled $CF_3O\cdot$ radicals, the origin of the $\tilde{A}^2A_1 \leftarrow \tilde{X}^2E$ transition was found to be at 28552 cm^{-1} and three fundamentals in the electronic excited state $\nu_3 = 635$, $\nu_5 = 626$, and $\nu_6 = 426$ cm^{-1} have been detected.[9] From the rotational fine structure of the transitions it was concluded that $CF_3O\cdot$ maintains C_{3v} symmetry in both the ground and excited states.[8,9] In early dispersed fluorescence spectra, three fundamental vibrations of $CF_3O\cdot$ have been observed in the electronic ground state at around 1250, 940, and 490 cm^{-1}, but with high uncertainties.[17,18] Very recently, five fundamentals, Jahn−Teller, and spin−orbit coupling constants of high accuracy in the ground state have been determined from dispersed fluorescence spectroscopy on jet-cooled $CF_3O\cdot$ radicals.[10]

The kinetics of many reactions, for example, between $CF_3O\cdot$ and $\cdot NO$,[19] $\cdot NO_2$,[20] CH_4,[18] or C_2H_6 [18] has been studied by gas flow laser induced fluorescence techniques. While the reaction with $\cdot NO$ produces CF_2O and FNO, which represents a major sink for $CF_3O\cdot$,[19] its reaction with $\cdot NO_2$ produces CF_3ONO_2, which was viewed as a temporary reservoir for $CF_3O\cdot$ in the atmosphere.[20] However, very recently it has been demonstrated that CF_3ONO_2 is also a sink for $CF_3O\cdot$ radicals, because its thermal decay occurs unimolecularly into $CF_2O + FNO_2$.[21] In all of the above-mentioned experimental studies the $CF_3O\cdot$ radicals were mostly generated either by excimer laser photolysis (λ = 193 nm) of CF_3OF or CF_3OOCF_3 [8,9,18] by thermal dissociation of CF_3OOCF_3,[20] or by IR multiphoton excitation with a CO_2 laser.[17]

Because $CF_3O\cdot$ is an open-shell Jahn−Teller active molecule, the theoretical prediction of its molecular properties is not an easy task. In a series of theoretical studies using ab initio and DFT methods, the geometries and vibrational frequencies of $CF_3O\cdot$ in the ground[15,22,23] and the first excited electronic states[15,24] have been reported. An electron affinity of 4.1 eV,[23] an activation energy of 35.3 kcal mol^{-1} for the dissociation into $CF_2O + F$,[25] and the Jahn−Teller parameters[22] have also been predicted. All these calculated properties are very helpful in the interpretation of experimental work.

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* Corresponding author.

[†] Alexander von Humboldt fellow. Permanent address: INFIQC Departamento de Físico-Química, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, 5000 Córdoba, Argentina.

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To collect more experimental spectroscopic data for CF_3O•, which provide a key to its structure, bonding, and chemistry, we decided to perform a matrix isolation study with the following objectives: (i) to measure a more complete IR spectrum, (ii) to record the so far unknown UV spectrum, and (iii) to evaluate the photochemical behavior.

Matrix isolated radicals can be produced in excellent yields by low-pressure pyrolysis of thermally labile precursors, which are highly diluted in argon or neon, followed by quenching of the products and the noble gas as a matrix at low temperatures. Recent examples of this approach are FCO_2•,[12] CF_3OO•, and FC(O)OO•,[11] formed by dissociation of the precursors FC(O)OOC(O)F, CF_3OONO_2, and FC(O)$OONO_2$, respectively.

Potential precursors for the formation of trifluoro methoxy radicals are CF_3OOCF_3,[26] $CF_3OOC(O)F$,[27] CF_3OOOCF_3,[28] $CF_3OOC(O)OCF_3$,[29] and $CF_3OC(O)OOC(O)OCF_3$.[30] The latter two are the most thermally labile species, which have allowed us to perform this study.

Experimental Section

The peroxides and trioxides used in this study are potentially explosive, especially in the presence of oxidizable materials. It is important to take safety precautions when these compounds are handled in the liquid or solid state.

General Procedures and Reagents. Volatile materials were manipulated in a glass vacuum line equipped with two capacitance pressure gauges (221 AHS-1000 and 221 AHS-10, MKS Baratron, Burlington, MA), three U-traps, and valves with PTFE stems (Young, London, U.K.). The vacuum line was connected to an IR cell (optical path length 200 mm, Si windows 0.5 mm thick) contained in the sample compartment of the FTIR instrument. This allowed us to observe the purification processes and to follow the course of reactions. The CF_3O• precursors CF_3OOCF_3,[26] CF_3OOOCF_3,[28] $CF_3OOC(O)F$,[27] $CF_3OOC(O)OCF_3$,[30] and $CF_3OC(O)OOC(O)OCF_3$[30] were prepared according to literature procedures and stored in flame-sealed glass ampules under liquid nitrogen in a long-term Dewar vessel. By using an ampule key,[34] the ampules were opened on the vacuum line, appropriate amounts were taken out for the experiments, and then they were flame-sealed again. The following chemicals were obtained from commercial sources: CF_2O (99%, Baker, Philipsburg, NY), Ar (99.999%) and Ne (>99.99%) (Messer Griesheim, Krefeld, Germany). These were used without further purification.

Preparation of Matrices. As $CF_3OC(O)OOC(O)OCF_3$ decomposed slowly at room temperature in vacuum lines, small amounts of the compound (ca. 0.1 mmol) were transferred in vacuo into a small U-trap immersed in liquid nitrogen. This U-trap was mounted in front of the matrix support (a metal mirror) and maintained at a temperature of −85 °C (ethanol bath). A gas stream (∼3 mmol h^{-1}) of argon or neon was directed over the cold sample in the U-trap, and the resulting gas mixtures passed the heated quartz nozzle (4 mm i.d., with an end orifice of 1 mm, heated zone length 20 mm) within milliseconds, being quenched subsequently on the matrix support at 12 or 5 K, respectively. Because the vapor pressures of the samples in the cold U-trap were approximately 10^{-3} mbar and the pressures of the inert gas streams during the deposition were about 1 mbar in the U-trap, the resulting sample-to-gas ratios could be estimated to be 1:1000. Two different amounts of matrix material (1 and 3 mmol, respectively) were deposited through the heated nozzle at a temperature of 300 °C. Mixtures of CF_2O, CO_2, CF_3OOCF_3, $CF_3OOC(O)F$, CF_3OOOCF_3, or $CF_3OOC(O)OCF_3$ with Ne or Ar in a molar ratio of about 1:1000 were prepared in a stainless steel high-vacuum line, transferred via a stainless steel capillary to the heated nozzle, and quenched as a matrix at 5 K or 12 K, respectively. For $CF_3OOC(O)OCF_3$, a nozzle temperature of 350 °C and for all other precursors a temperature of 500 °C was adjusted. IR matrix spectra of all precursors without pyrolysis as well as of CF_2O and CO_2 were recorded for use as references and to allow digital spectra subtractions.

Photolysis experiments on the matrices were undertaken in the visible and UV regions by using a 250 W tungsten halogen lamp (Osram, München, Germany) or a high-pressure mercury lamp (TQ 150, Heraeus, Hanau, Germany), respectively, in combination with cutoff and interference filters (Schott, Mainz, Germany). Details of the matrix apparatus have been described elsewhere.[12]

Instrumentation. *IR Spectroscopy.* Gas-phase infrared spectra were recorded with a resolution of 2 cm^{-1} in the range of 4000−400 cm^{-1} using the FTIR instrument (Nicolet, Impact 400 D, Madison WI), which was directly coupled to the vacuum line. Matrix IR spectra were recorded on a IFS 66v/ FT spectrometer (Bruker, Karlsruhe, Germany) in the reflectance mode using a transfer optic. A DTGS detector together with a KBr/Ge beam splitter operated in the regions of 5000−400 cm^{-1}. In these regions, 64 scans were co-added for each spectrum using apodized resolutions of 1.0 cm^{-1}. A far-IR DTGS detector together with a 6 μm Mylar beam splitter were used in the region of 500−80 cm^{-1}. In this region, 64 scans were co-added for each spectrum using an apodized resolution of 1.0 cm^{-1}.

UV Spectroscopy. UV spectra were recorded in the region 230−360 nm with a 1024 diode array spectrometer (Spectroscopy International) equipped with a deuterium lamp and two quartz single fibers of 2 m length with a special condensor (Hellma, Jena, Germany). Measurements with a 300 grooves mm^{-1} grating allowed a spectral resolution of 0.8 nm. A Hg pen lamp (Oriel) was used for wavelength calibration.

Results and Discussion

CF_3O• radicals are obtained by low pressure pyrolysis of different thermally labile precursors, which are highly diluted in inert gases. For each experiment, the gas stream doped with the precursor is passed through a heated nozzle. After the expansion of the products into high vacuum, the gas mixture is immediately quenched as a low-temperature matrix. The experimental setup is similar to that described in a study on FCO_2• radicals.[12] CF_3OOCF_3,[26] CF_3OOOCF_3,[28] $CF_3OOC(O)F$,[27] $CF_3OOC(O)OCF_3$,[29] and $CF_3OC(O)OOC(O)OCF_3$ [30] are chosen as precursors. Best yields with little amount of secondary products are obtained by using $CF_3OOC(O)OCF_3$ and $CF_3OC(O)OOC(O)OCF_3$. The primary thermal dissociation reactions can be formulated as

$$CF_3OOC(O)OCF_3 \xrightarrow{\Delta} 2CF_3O\bullet + CO_2 \qquad (1)$$

$$CF_3OC(O)OOC(O)OCF_3 \xrightarrow{\Delta} 2CF_3O\bullet + 2CO_2 \qquad (2)$$

Because CF_3OOCF_3, CF_3OOOCF_3, and $CF_3OOC(O)F$ are the most stable in this series of compounds, they are found to be inefficient precursors for CF_3O• radicals. They are only partially dissociated at the maximum temperature allowed for the pyrolysis device (500 °C) and secondary reactions such as

$$CF_3O\bullet \xrightarrow{\Delta} CF_2O + F\bullet \qquad (3)$$

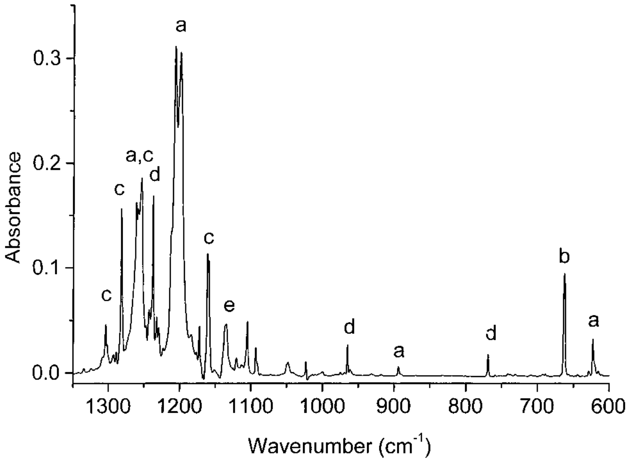

Figure 1. Spectrum of the pyrolysis products of $CF_3OC(O)OOC(O)OCF_3$ isolated in an argon matrix. The origins of the bands are (a) $CF_3O•$, (b) CO_2, (c) CF_3OOCF_3, (d) CF_2O, (e) unknown.

strongly reduce the yield of $CF_3O•$. In accordance with earlier attempts,[31] the pyrolysis of CF_3OOCF_3 results only in minor amounts of $CF_3O•$ radicals, because the O−O bond strength of 46.8 kcal mol^{-1} in CF_3OOCF_3 [32] is higher than the activation energy of 35.5 kcal mol^{-1} for the thermal dissociation of $CF_3O•$[25] according to eq 3.

Dimerization of $CF_3O•$ radicals according to

$$2CF_3O• + M \rightarrow CF_3OOCF_3 + M \tag{4}$$

also reduces the yield of $CF_3O•$ radicals. To minimize this reaction, high dilution of the precursors (e.g., Ar:$CF_3OC(O)OOCF_3$ > 1000:1) and a proper flow rate (~2 mmol h^{-1}) of the gas mixture have to be used to maintain an optimum pressure and residence time inside the pyrolysis zone of the heated spray-on nozzle.

It is surprising that CF_3OOCF_3 has been described as a good thermal source for $CF_3O•$ radicals by Caralp et al.,[20] because in low-pressure pyrolysis experiments performed by us and others,[31] only minor amounts of $CF_3O•$ were formed. The reason for this discrepancy is found in differences in the experimental setup for both pyrolysis devices. Presumably Caralp et al.[20] used a "high pressure" (1−200 mbar CF_3OOCF_3) pyrolysis device (unfortunately the experimental details are poorly described). Under high pressure conditions, presumably a steady-state concentration of $CF_3O•$ radicals is maintained in equilibrium with CF_3OOCF_3. The rate-determining step—the unimolecular decomposition of the $CF_3O•$ radicals (3)— is itself retarded by inhibition with the end product CF_2O.[33]

The IR Spectrum of CF_3O. Only one single IR-absorption around 1220 cm^{-1} of matrix isolated $CF_3O•$ is known from the literature.[14,16] We are able to confirm this observation by using CF_3OOCF_3, CF_3OOOCF_3, or $CF_3OOC(O)F$ as starting materials as described above. However, the use of $CF_3OOC(O)OCF_3$ or $CF_3OC(O)OOC(O)OCF_3$ results in much higher yields of $CF_3O•$ radicals and more fundamentals become observable. A typical IR-spectrum of the pyrolysis products of $CF_3OC(O)OOC(O)OCF_3$ is depicted in Figure 1. The primary byproduct CO_2 (b), the dimerization product CF_3OOCF_3 (c), and the decomposition product CF_2O (d) are identified by reference spectra. The unknown band labeled (e) is either absent or of low intensity when different precursors and pyrolysis conditions are used. All new bands (a) that appear in each experiment with a constant intensity ratio and decrease in intensity after UV photolysis (λ > 280 nm, see Figure 2) are attributed to $CF_3O•$ radicals. The main photoproducts are CF_2O molecules and fluorine atoms. The latter escape from the matrix cage and are IR inactive. Additional minor IR bands are either due to photoproducts from impurities (e.g., CO_2 from the starting material) or to incomplete compensation after digital spectra subtraction. In all photolysis experiments on matrices containing $CF_3O•$ there appears a small band near 660 cm^{-1} that is hidden under the strong CO_2 absorption of the initial IR spectrum (Figure 1). Nevertheless, this band is always present in the difference spectra (see Figure 2). By comparison with the predicted IR spectrum presented in Table 1, we believe that this band is a fundamental.

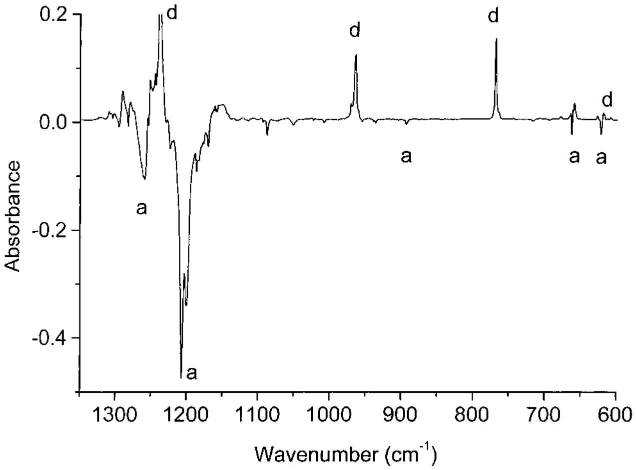

Figure 2. Difference IR spectrum after photolysis (1 h) of $CF_3O•$ isolated in an argon matrix with UV light of wavelength λ > 34000 cm^{-1}. Bands of the photoproduct CF_2O (d) are pointing upward and those of the decomposed $CF_3O•$ radicals (a) are pointing downward.

TABLE 1: Vibrational Wavenumbers (cm^{-1}) of the $CF_3O•$ Radical in the $\tilde{X}\ ^2A'$ Ground State

calcd for C_s symmetry[a]			experimental			gas phase[c]	C_s sym assignment
B3LYP	BHLYP	I	Ne	Ar-matrix	I[b]		
1252	1356	82	1273	1260	55	1215 (A_1)	ν_1(A), ν(CO)
1200	1316	100	1215	1207	90	(E)[d]	ν_7(A″,ν(CF)
1164	1303	86	1207	1199	100		ν_2(A′), ν(CF)
886	944	0.7	891	894	1	977 (A_1)	ν_3(A′), ν(CF)
608	646	3.2	666	663	2	600 (E)	ν_4(A′), $\delta(CF_3)$
585	621	0.7					ν_8(A″), twist CF_2
566	605	2.8	621	622	3	527 (A_1)	ν_5(A′), scissor CF_2
396	429	0.2				465 (E)	ν_6 (A′), δ(OCF)
252	253	0.5					ν_9 (A″), rock CF_2

[a] From ref 23, the most intensive band for BHLYP is 433 km mol^{-1}. [b] Relative integrated intensities. [c] Deduced from the dispersed fluorescence spectrum of the $\tilde{A}^2A_1 \rightarrow \tilde{X}^2E$ transition, assignment according to C_{3v} symmetry of the $\tilde{X}^2E$ ground state in the gas phase, ref 10. [d] In ref 10 not observed.

A descriptive picture about the ab initio geometries and energetics of $CF_3O•$ is given in ref 3. The degenerate unstable ground state $\tilde{X}^2E$ (C_{3v}) is relaxed into a transition structure $\tilde{X}^2A''$-(C_s) by 0.28 kcal mol^{-1} and into the equilibrium structure $\tilde{X}^2A'$ (C_s) by 0.33 kcal mol^{-1}. In the equilibrium structure, the O-atom is tilted away from the C_3 axis and the single occupied oxygen p-orbital lies in the mirror plane. The irreducible representations of the nine possible vibrational modes of $CF_3O•$ are dependent on its symmetry:

$$C_{3v}\colon \Gamma_{\text{vib}} = 3A_1(\text{IR, Ra p}) + 3E(\text{IR, Ra dp})$$

$$C_s\colon \Gamma_{\text{vib}} = 6A'(\text{IR, Ra p}) + 3A''(\text{IR, Ra, dp})$$

where p = polarized and dp = depolarized. If $CF_3O•$, exhibiting

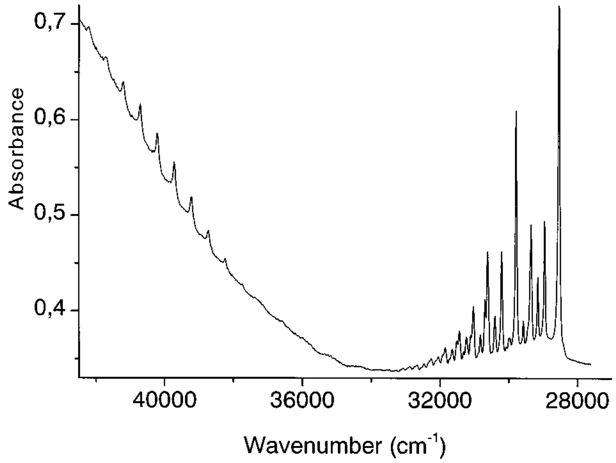

Figure 3. UV absorption spectrum of CF$_3$O• radicals isolated in a neon matrix.

C_{3v} symmetry, is distorted to C_s symmetry, the double degenerate E modes will split into A′ and A″ components. Hence, the observed splitting of the asymmetric CF$_3$ stretching mode indicates C_s symmetry for the matrix isolated CF$_3$O• radicals.

On several levels of theory, the vibrational wavenumbers of CF$_3$O• in the equilibrium structure $\tilde{X}^2$A′ (C_s) have been calculated[23] and the most reliable results are presented in Table 1. Because the calculated vibrational band positions and band intensities match the experiment reasonably well, this is a further proof that matrix-isolated CF$_3$O• possesses C_s symmetry in the electronic ground state. This finding is at variance with the conclusions drawn from the simulation of the rotational resolved dispersed-fluorescence spectra, where C_{3v} symmetry for gaseous CF$_3$O• in the ground state is found.[10] A key for the understanding of this discrepancy may be the unusual deviation between gas phase and matrix IR wavenumbers indicating a strong interaction of CF$_3$O• radicals with the host atoms. This interaction may increase the Jahn−Teller stabilization energy so as to lock CF$_3$O• into a permanent distortion.

The other unusual feature of the IR spectrum, the broad absorptions in the region of 1150−1300 cm^{-1}, may be due to vibronic Jahn−Teller coupling.

The UV Spectrum of CF$_3$O•. The UV spectrum of CF$_3$O• radicals isolated in a neon matrix is presented in Figure 3. For a five-atomic species, the appearance of a well-structured UV-spectrum is quite unusual. By comparison, CF$_3$OO• shows just a broad, structureless UV-spectrum.[11] At least two different electronic transitions must be involved. One of them extends from 28000 to 34000 cm^{-1} and the other from 34000 cm^{-1} to higher wavenumbers. At the high-frequency end of the spectrum, the absorptions of the byproducts CO$_2$, CF$_3$OOCF$_3$, and CF$_2$O contribute above 42000 cm^{-1}. The high energy band shows a single vibrational progression spanning around 495 ± 10 cm^{-1} between the peaks. In several former studies, a small part of the low energy transition has been probed (28500 to 29800 cm^{-1}) by tuneable lasers and fluorescence excitation spectra have been observed.[8,9,17,18] However, the intensity pattern of the fluorescence excitation spectra, which decreases strongly in intensity to higher wavenumbers, is different from our absorption spectrum. Hence we conclude that with increasing energy the UV absorption becomes more and more dissociative and the fluorescence probability decreases. This interpretation is in accordance with the photochemical behavior of matrix-isolated CF$_3$O• radicals. Irradiation of the matrix with UV-light of λ > 34000 cm^{-1} causes slow decomposition into CF$_2$O + F (see above).

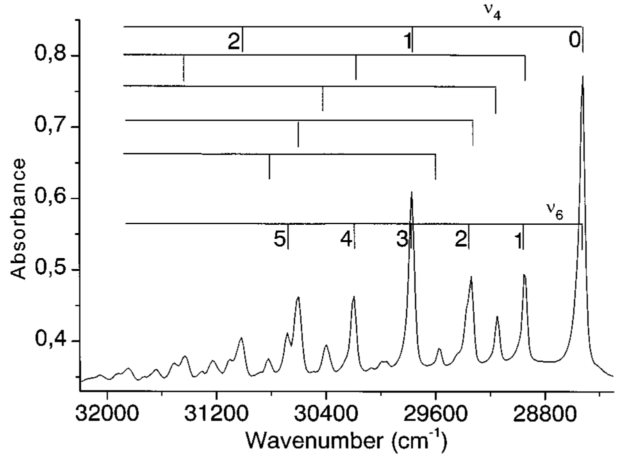

Figure 4. Part of the UV absorption spectrum of CF$_3$O• ($\tilde{A}^2$A$_1$ ← $\tilde{X}^2$E transition) with assignments of the most prominent progressions.

The low energy UV absorption is assigned to a $\tilde{A}^2$A$_1$ ← $\tilde{X}\,^2$E transition,[15] and the structure is due to different vibrational progressions in the excited state. The three vibrations $\nu_3 = 635$, $\nu_5 = 626$, and $\nu_6 = 426$ cm^{-1} observed in the excitation fluorescence spectrum of jet cooled CF$_3$O• radicals[9] are also present in the neon matrix UV spectrum. Figure 4 shows an enlarged part of the low energy band. The transition centered at 28951 cm^{-1} corresponds to a vibrational mode of 434 cm^{-1} (ν_6) above the origin at 28517 cm^{-1}. The next line lying at 29149 cm^{-1} constitutes the transition from the ground to the excited state of the second fundamental at 632 cm^{-1}. The corresponding band in the gas phase consists of two little separated bands ν_3 and ν_5, but they are not resolved in the matrix spectrum because the line widths of the transitions in neon matrix are about 40 cm^{-1}. Therefore, the labeling of transitions containing the component 632 cm^{-1} will be throughout ν_3/ν_5 in Table 2. In Tables 2 and 3 it is suggested that there are four fundamentals involved and that they progress along the spectrum by acquiring additional excitation from the 1254 cm^{-1} (ν_4) mode. To illustrate this, the most prominent progressions are indicated in Figure 4. Even the "combination" at 1060 cm^{-1} ($\nu_6 + \nu_3/\nu_5$) from the origin can be thought of as gaining energy when acquiring a quantum in ν_4. Because no unique description of all features can be accomplished, a set of possible alternative band assignments is presented in Table 2. They include spectral lines lying within ±20 cm^{-1} from each measured peak. The uncertainty of band positions is estimated to be ±3 cm^{-1}, and that of the deduced vibrational wavenumbers in Table 3 is ±5 cm^{-1}. Compared to the gas phase, in the neon matrix the band origin is 35 cm^{-1} red shifted and there is an excellent agreement between gas phase and matrix vibrational frequencies in contrast to the values in the electronic ground state (see Table 1).

Our band assignment, which has neglected any correction due to anharmonicity, shows that several possible excitations exist. Among these, the one that corresponds to the excitation of ν_6, a bending of the OCF angle is the only one that shows a progression to high quantum numbers. This behavior has also been observed for the FCO$_2$• radical[12] and is entirely consistent with different geometries in both the ground and excited states. In the ground state, the radical has C_s symmetry due to the enhanced Jahn−Teller effect in the matrix. During excitation, an electron from a filled sp hybrid-type orbital symmetric with respect to the C−O bond is promoted to the partially filled π-type orbital. The major effect is to decrease the C−O bond strength, resulting in a lengthening of the C−O bond and

TABLE 2: Energies (cm^{-1}) in the $\tilde{A}^2A_1 \leftarrow \tilde{X}^2E$ Transition Containing Various Progressions of $CF_3O\cdot$ Isolated in Neon Matrix

ν_2	ν_3/ν_5	ν_4	ν_6	calcd[a]	obsd[b]
0	0	0	0	28517	28517
0	0	0	1	28951	28951
0	1	0	0	29149	29149
1	0	0	0	29336	29336
0	0	0	2	29385	29374
0	1	0	1	29583	29577
0	0	1	0	29771	29771
1	0	0	1	29770	29771
{0	2	0	0	29781	29771}
{0	0	0	3	29819	29967}
{0	1	0	2	30017	29993}
{2	0	0	0	30155	30192}
0	0	1	1	30205	30192
1	0	0	2	30204	30192
0	0	0	4	30253	30192
0	1	1	0	30403	30394
{1	1	0	1	30402	30394}
{2	0	0	1	30589	30598}
{1	2	0	0	30600	30598}
0	0	1	2	30629	30598
0	0	0	5	30687	30681
{2	1	0	0	30787	30826}
0	1	1	1	30826	30837
1	0	1	1	31024	31016
{0	2	1	0	31035	31016}
0	0	0	6	31121	31100
{1	1	1	0	31222	31229}
{0	1	0	5	31319	31301}
{2	0	1	0	31409	31431}
0	0	2	1	31459	31431
{1	0	0	5	31506	31503}
{0	1	2	0	31657	31635}
{1	1	1	1	31656	31635}
{1	1	0	4	31704	31723}
{0	1	0	6	31753	31723}
1	0	2	0	31844	31842
{0	0	1	5	31941	31916}
{0	1	1	4	32139	32127}
{1	0	1	4	32326	32250}

[a] Assignments in brackets are tentative. [b] Where band positions are repeated, several transitions are overlapping.

TABLE 3: Parameters (cm^{-1}) for the CF_3O Radical in the $\tilde{A}^2A_1$ Excited State

calcd		exptl		C_{3v} sym assignment
IP6-31G(d,P)[a]	RHF/3-21G[b]	gas phase[c]	neon matrix	
32700	29500[d]	28552	28517	ν_{00}
1030	887			ν_1 (A_1)
907	801		819	ν_2 (A_1)
660	631	635	632	ν_3 (A_1)
1319	1326		1254	ν_4 (E)
648	611	626	632	ν_5 (E)
446	409	426	434	ν_6 (E)

[a] Reference 24. [b] Reference 15. [c] Reference 9. [d] Reference 17.

lowering of the C−O stretching frequency in the excited state. This lengthening allows also the OCF bond angle to decrease.

Conclusion

Very efficient precursors have been found for the thermal formation of $CF_3O\cdot$ radicals under matrix isolation conditions. Hence, it was possible to measure its UV spectrum in the region 230−360 nm for the first time and to record its complete IR spectrum with detection of new fundamentals. The gas-phase data of the fluorescence excitation spectra[8−10,17,18] are in general agreement with the UV matrix data. However, there are disagreements between the gas-phase fundamentals in the electronic ground state, deduced from the dispersed fluorescence spectrum,[10] and the IR matrix data. This may be due to the fragile structure of $CF_3O\cdot$. In matrix, it is permanently Jahn−Teller distorted by interaction with the host atoms.

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