Contribution from the Soreq Nuclear Research Center, Yavne, Israel, and Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem, Israel

Reaction of Ammonium Pertechnetate with Anhydrous Hydrogen Fluoride. Vibrational Spectra of Pertechnetyl Fluoride

J. BINENBOYM, U. EL-GAD, and H. SELIG*

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Ammonium pertechnetate dissolves slightly in anhydrous hydrogen fluoride to give solutions of pertechnetyl fluoride. Raman spectra of the solutions as well as infrared and Raman spectra of the pure compound indicate that TcO_3F has symmetry C_{3v} with the following assignments (in cm^{-1}): (a_1) 696, 962, 317; (e) 951, 347, 231. A comparison with other MO_3X compounds indicates a necessity to reverse some of the original assignments.

Introduction

The reaction of hydrogen fluoride with oxides is an acknowledged method for preparing fluorides and oxyfluorides which are not easily susceptible to hydrolysis.[1] If the resulting product is, however, readily hydrolyzed, then this preparative method is considered unsuitable because the water formed as a by-product would interfere. Such an assumption was made in the case of the reaction of potassium perrhenate with hydrogen fluoride, for example.[2] Recently we have shown that in the presence of an excess of anhydrous hydrogen fluoride (AHF), the water formed is tied up, and the resulting solutions contain perrhenyl fluoride as attested to by their Raman spectra.[3] We have now found that an analogous reaction occurs between ammonium pertechnetate and AHF to form solutions of pertechnetyl fluoride. In order to demonstrate this conclusively, we have prepared pertechnetyl fluoride directly and compared its spectra with those of the AHF solutions.

Experimental Section

Materials. Anhydrous hydrogen fluoride was purified by distillation in a column described previously.[4] The resulting distillate had a conductivity of 10^{-5}–10^{-6} ohm^{-1} cm^{-1} at 0°. Ammonium pertechnetate was obtained as the dry salt from the Oak Ridge National Laboratories. The salt as received was black and not completely water soluble. It was leached with distilled water which was then filtered and evaporated to dryness in the presence of excess ammonia. The resulting white salt was then either dissolved in anhydrous HF or decomposed to TcO_2 in dry nitrogen flow at 300°. Pertechnetyl fluoride was prepared[5] by heating the TcO_2 in a fluorine stream at 400 mm pressure and 150°. The TcO_3F formed had the properties ascribed to it previously.[5]

Apparatus. Raman spectra were recorded using a Spex 1401 monochromator and Spex 1419A sample illuminator. The scattered radiation was collected at 90° and focused by an $f/0.95$ lens on the entrance slit after passing through an analyzer and a polarization scrambler. Method of detection was photon counting using a thermoelectrically cooled selected RCA C31034 GaAs photomultiplier. Irradiation was by means of a Spectra Physics Model 125 He–Ne laser yielding about 50-mW power at the sample. Spectra were calibrated by reference to emission lines of neon using the laser plasma lines which appeared upon removing the interference filter. Liquid samples were contained in $^1/_4$- or $^3/_{16}$-in. Teflon FEP tubes as described elsewhere.[6] Polarization measurements were made by method VII of those listed by Claassen, Selig, and Shamir,[7] except for those on the NH_4TcO_4–HF solutions which were obtained on another instrument using method III.

Infrared spectra of TcO_3F vapor were recorded on a Beckman Model 20A spectrophotometer (250–4000 cm^{-1}) using a 10-cm nickel cell with silver chloride or polyethylene windows. In addition, the range 400–200 cm^{-1} was covered by measurements on a Perkin-Elmer 621 spectrophotometer. The cells were preconditioned by treatment with chlorine trifluoride vapor. Background scans were obtained by scanning over the spectrum with the sample contained in a side arm maintained at liquid nitrogen temperature. Additional spectra were obtained with the side arm held at 0 and 20°. Intensities were limited by the relatively low vapor pressure of the compound (24 mm at 20°). A final background spectrum was obtained by refreezing the sample into the side arm, thus ascertaining that none of the peaks were due to material on the windows. Infrared spectra were calibrated by reference to water and CO_2 lines in a superimposed single-beam spectrum. Values are good to ±2 cm^{-1}.

Fluorine nmr spectra were obtained on a Varian HA-100 spectrometer operating at 94.1 MHz. Nmr samples were made up in $^3/_{16}$-in. o.d. FEP tubes, which were sealed under vacuum. Chemical shifts were measured with respect to CCl_3F as an external reference.

Results and Discussion

Ammonium pertechnetate dissolves sparingly in AHF to yield a pale yellow solution with an undissolved solid layer at the bottom. It is much less soluble than potassium perrhenate, but because of technical difficulties engendered by its radioactivity, the solubility of the pertechnetate was not determined. The Raman spectrum of the solution (Figure 1) was measured on an apparatus previously described.[7] Because of the high gains necessary to obtain reasonable intensities, it was not possible to eliminate completely some of the FEP lines even with a shortened slit height. The close similarity of the spectrum to that of ReO_3F[3] shows that TcO_3F is formed in an HF solution. The spectrum is, moreover, nearly identical except for some minor frequency shifts to that of neat TcO_3F liquid (Figure 2). A mixture of TcO_3F with HF forms a two-phase liquid system at room temperature with a low concentration of TcO_3F in the upper layer. This HF layer yielded a Raman spectrum identical with that of an NH_4TcO_4–HF solution.

The TcO_3F molecule, by comparison with the perrhenyl halides, would be expected to possess C_{3v} symmetry. For this structure there must be six fundamentals—all infrared and Raman active. Three of these are totally symmetric vibrations of species a_1 and three are doubly degenerate vibrations of species e. The numbering of fundamentals in our discussion will be in accordance with the convention of Siebert.[8]

Two Raman bands, one polarized and one depolarized, are

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* To whom correspondence should be addressed at Hebrew University.

(1) E. L. Mutterties and C. W. Tullock, *Prep. Inorg. React.*, 2, 270 (1965).

(2) A. Engelbrecht and A. V. Grosse, *J. Amer. Chem. Soc.*, 76, 2042 (1954).

(3) H. Selig and U. El-Gad, *J. Inorg. Nucl. Chem.*, 35, 3517 (1973).

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(6) M. Brownstein and J. Shamir, *Appl. Spectrosc.*, 26, 77 (1972).

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(8) H. Siebert, "Anwendungen der Schwingungspektroskopie in der anorganischen Chemie," Springer-Verlag, Berlin, 1966, p 71.

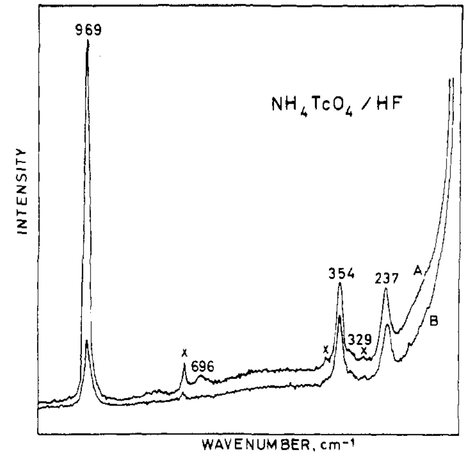

Figure 1. Raman spectra of solutions of NH_4TcO_4 in AHF. Incident light polarized: (A) perpendicular and (B) parallel to plane containing the slit and the laser beam; spectral slit width 8 cm^{-1}. x = FEP lines.

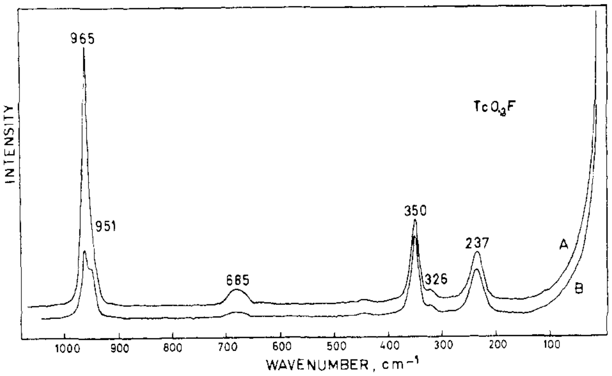

Figure 2. Raman spectra of TcO_3F liquid. Scattered light polarized: (A) perpendicular and (B) parallel to plane containing slit; spectral slit width 6 cm^{-1}.

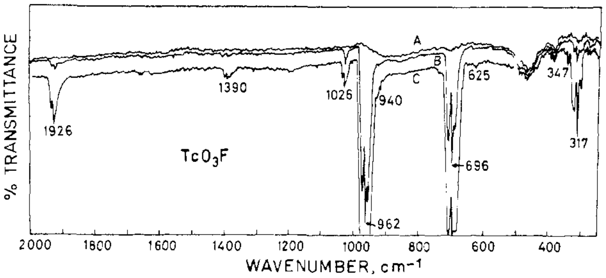

Figure 3. Infrared spectrum of TcO_3F gas, obtained on a Beckman 20A spectrophotometer: (A) background; (B) 4-Torr pressure; (C) 24-Torr pressure.

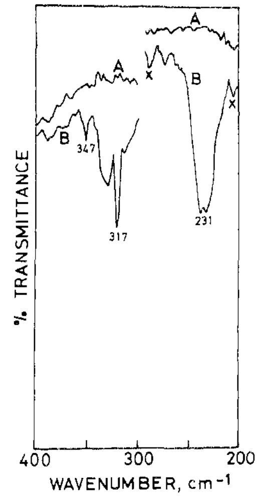

Figure 4. Infrared spectrum of TcO_3F gas, obtained on a Perkin-Elmer 621 spectrophotometer: upper trace, background; lower trace, 24-Torr pressure.

Table I. Infrared and Raman Frequencies (cm^{-1}) of TcO_3F

Infrared		Raman		
Freq	Intens[a]	Liquid	NH_4TcO_4-HF soln	Assignment
1926	w			$2\nu_2 = 1924$
1390	vw			$2\nu_1 = 1392$
1026	w			SiF_4 (?)
971				
962	vs	965 p	969 p	$\nu_2(a_1)$
953				
~940	w	951 dp		$\nu_4(e)$
706				
696	s	685 p	696 p	$\nu_1(a_1)$
684				
625	vw			$2\nu_3 = 634$
445	vvw			$2\nu_6 = 462$
347	w	350	354	$\nu_5(e)$
327				
317	m	326	329	$\nu_3(a_1)$
308				
231	ms	237	237	$\nu_6(e)$

[a] Key: s, strong; ms, medium strong; m, medium; w, weak; vw, very weak.

observed in the neat liquid at 965 and 951 cm^{-1} in the frequency range expected for Tc-O bond stretching motions. These are therefore assigned unambiguously as ν_2 and ν_4, the Tc-O symmetric stretch (a_1) and the asymmetric stretch (e), respectively. Their relative intensities, depolarization factors, and positions are characteristic of the pyramidal group TcO_3 and are nearly identical with those found for the terminal TcO_3 groups in the molecules TcO_3Cl[9] and Tc_2O_7.[10] Infrared spectra of TcO_3F vapor are shown in Figures 3 and 4. These confirm the coincidences with the Raman spectra. A strong absorption with a characteristic PQR structure occurs at 962 cm^{-1}. At high intensities a weak shoulder can be seen on the low-frequency side of this absorption band. It probably belongs to the Tc-O asymmetric stretching mode. The two frequencies are not resolved well in the Raman spectrum, but in the depolarized scan the decrease in intensity of the a_1 fundamental causes the e fundamental to be more prominent. In the spectra on the HF solutions the two bands are nearly superimposed, but an abscissa expansion shows the peak to be definitely skewed toward the low-frequency side. The exact location of the lower frequency peak was obtained by computer deconvolution of this two-band system.

Only one other polarized band is observed in the Raman spectrum at 686 cm^{-1}, and by analogy with ReO_3F, this is assigned to the Tc-F stretching mode ν_1. This Raman band appears somewhat broader and differently shaped from the other bands. It may contain an overtone of the medium-intensity fundamental at 350 cm^{-1}. Although these are of the same symmetry and thus Fermi resonance would be allowed, there is no evidence of this occurring. The corresponding infrared absorption appears as a PQR band centered at 696 cm^{-1}. The lowest frequency band observed in the Raman spectrum at 238 cm^{-1} and in the infrared spectrum

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(10) H. Selig and S. Fried, *Inorg. Nucl. Chem. Lett.*, 7, 315 (1971).

Table II. Vibrational Assignments of MO_3X Molecules (M = Re, Tc)

Fundamental	Species	TcO_3F^a	TcO_3Cl^b	ReO_3F^c	ReO_3Cl^d	ReO_3Br^e	Description of Mode
ν_1	a_1	696	445	666	435	195	M-X str
ν_2	a_1	962	950	1009	1001	997	MO_3 sym str
ν_3	a_1	317	299	321	303	332	MO_3 sym def
ν_4	e	951	932	980	961	963	MO_3 asym str
ν_5	e	347	340	403	344	350	MO_3 asym def
ν_6	e	231	197	174	196	168	X-M-O rock

[a] This work. [b] Reference 9, but with ν_1 and ν_3 reversed. [c] Reference 3, but with ν_3 and ν_5 reversed. [d] References 9 and 12, but with ν_1 and ν_3 reversed. [e] Reference 12, but with ν_3 and ν_5 reversed. The assignments for ReO_3Br are tentative only (see text.)

at 231 cm^{-1} can be assigned to the F-Tc-O rocking mode. The remaining two bands at 317 and 347 cm^{-1} cannot be assigned with absolute certainty. However, in the infrared spectrum (Figure 4), the band at 317 cm^{-1} has a parallel band structure with PQR maxima while the one at 347 cm^{-1} appears to be a perpendicular band. We accordingly assign these bands as $\nu_3(a_1) = 317$ cm^{-1} and $\nu_5(e) = 347$ cm^{-1}. The observed ir and Raman frequencies of TcO_3F are in Table I. There appear to be some inconsistencies in the assignments for analogous MO_3X molecules; a comparison of these molecules is therefore appropriate. A review of the vibrational assignments for molecules of this type has been given by Ngai and Stafford.[11] The frequencies assigned by them to the Re-Cl modes are not those of the original authors,[9,12] who preferred lower frequencies. They are consistent, however, with M-Cl modes in other transition metal oxychlorides and are supported by the theoretical calculations of Muller, *et al.*,[13] albeit the latter are based on somewhat arbitrary assumptions. By applying similar reasoning, the two assignments for ν_1 and ν_3 given by the original authors[9] for TcO_3Cl should also be reversed, as well as the assignments for ν_3 and ν_5 given originally[3] for ReO_3F. The overall picture then emerges that we have reasonable consistency of the MO_3 symmetric and asymmetric deformation modes, which should remain relatively constant for all of these molecules. In all instances the MO_3 symmetric deformation mode is lower in frequency than the MO_3 asymmetric deformation mode. A further consistency occurs in the more reasonable decrease of the M-X stretching frequencies from fluoride to chloride. Moreover in all cases ν_1 and ν_2 are strongly polarized while ν_3 is partially polarized for the chlorides, but not discernibly so for both fluorides. A summary for all known ReO_3X and TcO_3X molecules is given in Table II. A further comment is necessary with regard to ReO_3Br. Although Ngai and Stafford[11] reversed the original authors'[12] assignment for the Re-Br mode, we prefer with some reservation the original assignment but interchange the assignments for the ReO_3 symmetric and asymmetric modes in order to preserve the relative consistency of these modes throughout the series. The latter assignments are rather arbitrary, and the Re-Br frequency is indeed lower than expected, but for lack of supporting evidence a more detailed discussion is not warranted. No Raman data are available for ReO_3Br, but with the advent of laser Raman spectroscopy, a reinvestigation of this molecule is in order, as polarization measurements may help clear up the assignment problems.

The ^{19}F nmr spectrum of liquid TcO_3F gives a resonance signal at δ_{CCl_3F} +50.6 ppm while those of NH_4TcO_4-HF solutions show a very weak and broad signal at about −10 to −20 ppm. This is the first time that a resonance of a fluorine bonded to a technetium atom has been observed, this compound being the only known fluorine-containing species of heptavalent technetium. Coupling with the high-spin ($I = {}^9/_2$) technetium nucleus was not observed, possibly because of quadrupole relaxation.

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Registry No. TcO_3F, 42246-22-0; TcO_3Cl, 42246-23-1; ReO_3F, 42246-24-2; ReO_3Cl, 42246-25-3; ReO_3Br, 42246-26-4.

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