is qualitatively supported by the results of $^{18}O$-exchange studies between water and phosphorus acids; the first-order rate constants for exchange[11] decrease with increasing phosphorus oxidation state, $k(H_3PO_2) \gg k(H_3PO_3) \gg k(H_3PO_4)$. We anticipate that the acid-dependent aquation of the $Cr(O_4PH_2)^{2+}$ ion is even slower than that of $Cr(O_3PH_2)^{2+}$.

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(11) A. I. Brodskii and L. V. Sulima, *Dokl. Akad. Nauk SSSR*, **92**, 589 (1953); *Chem. Abstr.*, **48**, 5620*d* (1954).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WESTERN ONTARIO,
LONDON 72, ONTARIO, CANADA

# The Fluorine-19 Nuclear Magnetic Resonance Spectrum of the Hexafluoroantimonate(V) Ion

BY R. G. KIDD AND R. W. MATTHEWS*[1]

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The $^{121}Sb$ and $^{123}Sb$ nmr spectra of the octahedral hexafluoroantimonate(V) ion in solutions of $NaSbF_6$ or $SbF_5$ in 48% aqueous hydrofluoric acid are known[2-4] to consist of seven-line multiplets due to spin–spin coupling of $^{19}F$ with the antimony nucleus. The corresponding multiplet structure expected for the $^{19}F$ nmr spectrum of this species, however, has apparently not been observed. We have now obtained complete resolution of this spectrum using a solution of the silver(I) salt in acetonitrile. The 14-line spectrum consists of a sextet arising from coupling of $^{121}Sb$ ($I = {}^5/_2$) with $^{19}F$, superimposed on an octet due to coupling of $^{123}Sb$ ($I = {}^7/_2$) with $^{19}F$. The spectrum is shown in the figure together with the corresponding $^{121}Sb$ and $^{123}Sb$ nmr spectra obtained in this laboratory. The coupling constants determined from the $^{19}F$ spectrum are $J_{F-^{121}Sb} = 1934\ (\pm 15)$ Hz and $J_{F-^{123}Sb} = 1047\ (\pm 25)$ Hz. The ratio $J_{F-^{121}Sb}/J_{F-^{123}Sb}$ is 1.85 (±0.06), in good agreement with the ratio of the gyromagnetic ratios $\gamma_{121}/\gamma_{123} = 1.8466$. The relative intensities of any two components due respectively to coupling with $^{121}Sb$ and $^{123}Sb$ is approximately 2:1, as expected for the isotopes in their natural abundances ($^{121}Sb$, 57.2%; $^{123}Sb$, 42.8%). Although the symmetry of the intensity pattern is somewhat unsatisfactory (see Experimental Section), the overall line shape of the sextet is in qualitative agreement with that calculated by Suzuki and Kubo[5] for the nmr spectrum of a nucleus of spin $I = {}^1/_2$ coupled to a nucleus with spin $I = {}^5/_2$. The values of the coupling constants are in good agreement with those obtained from $^{121}Sb$ and $^{123}Sb$ nmr spectra by Hatton, *et al.* ($J_{F-^{121}Sb} = 1945\ (\pm 5)$ Hz; $J_{F-^{123}Sb} = 1055\ (\pm 5)$ Hz).[4,6] A value of $J_{F-^{121}Sb} = 1820$ Hz has also been determined from the $^{19}F$ nmr of solid $KSbF_6$.[7] The chemical shift of $AgSbF_6$ in acetonitrile, $\delta_{CFCl_3}$ +123 ppm, is within about 10 ppm of values found for absorptions previously assigned to $SbF_6^-$.[8-10]

Since $^{19}F$ nmr spectra previously reported for this ion have consisted of single absorptions with varying line widths, it was of interest to determine, qualitatively at least, the factors influencing resolution of the multiplet. For spin–spin coupling involving quadrupolar nuclei ($I > {}^1/_2$), the component line widths depend on the rate of quadrupole relaxation. Increase of either the electric field gradient around the high-spin nucleus or the rotational correlation time should increase the rate of relaxation and thus broaden the resonance lines.[11] For ionic species, the electric field gradient is expected to be sensitive to the magnitude of ion–ion interactions and hence to changes in dielectric constant ($\epsilon$) of the solvent and change of the counterion. Previous studies of the $^{19}F$ nmr of the hexafluoroarsenate(V)[12] and -niobate(V)[13-15] ions have demonstrated the dependence of multiplet resolution on these factors.

We have found similar results for $SbF_6^-$ in nonaqueous solution. The $^{19}F$ nmr of dilute solutions of $AgSbF_6$ in dimethyl sulfoxide ($\epsilon = 45.0$) and *N,N*-dimethylformamide ($\epsilon = 36.1$) showed resolution comparable to that for acetonitrile solution ($\epsilon = 38.0$), but noticeable broadening of the components occurred for dilute solutions in acetone ($\epsilon = 20.7$). The component line widths are also sensitive to change of cation. A solution of $NaSbF_6$ in acetonitrile, similar in concentration to that used to determine the $^{19}F$ spectrum of $AgSbF_6$ (~2 *M*), showed considerable broadening of both $^{19}F$ and $^{121}Sb$ multiplets. Saturated solutions of $AgSbF_6$ in dimethyl sulfoxide, *N,N*-dimethylformamide, and acetone were highly viscous and showed considerably broadened bands in their $^{19}F$ spectra, consistent with the increase in correlation time compared to dilute solutions. In the temperature range +50 to −40°, the $^{19}F$ spectra of the dilute solutions showed little change. The broad multiplets in the $^{19}F$ spectra of the viscous solutions, however, progressively coalesced to give somewhat sharper singlets as the temperature was lowered. The various line shapes were similar to those calculated by Suzuki, *et al.*[5] From these results, we conclude that, in nonaqueous solvents, multiplet resolution is mainly determined by solvent dependence of the rate of quadrupole relaxation.

Compared to their acetonitrile solutions, $AgSbF_6$ and $NaSbF_6$ in 48% aqueous hydrofluoric acid showed considerable broadening of the $^{19}F$ and $^{121}Sb$ multiplets.

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[1] Address correspondence to this author at the University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, England.

(2) W. G. Proctor and F. C. Yu, *Phys. Rev.*, **81**, 20 (1951).

(3) S. S. Dharmatti and H. E. Weaver, Jr., *ibid.*, **87**, 675 (1952).

(4) J. V. Hatton, Y. Saito, and W. G. Schneider, *Can. J. Chem.*, **43**, 47 (1965).

(5) M. Suzuki and R. Kubo, *Mol. Phys.*, **7**, 201 (1964).

(6) The instrumentation used to observe the antimony nmr spectra does not allow us to match the precision of the results quoted by these authors.

(7) E. R. Andrew, L. F. Farnell, and T. D. Gledhill, *Phys. Rev. Lett.*, **19**, 6 (1967).

(8) J. Bacon, P. A. W. Dean, and R. J. Gillespie, *Can. J. Chem.*, **48**, 3413 (1970).

(9) M. Azeem, M. Brownstein, and R. J. Gillespie, *ibid.*, **47**, 4159 (1969).

(10) E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, **81**, 1084 (1959).

(11) J. A. Pople, *Mol. Phys.*, **1**, 168 (1958).

(12) K. J. Packer and E. L. Muetterties, *Proc. Chem. Soc., London*, 147 (1964).

(13) K. J. Packer and E. L. Muetterties, *J. Amer. Chem. Soc.*, **85**, 3035 (1963).

(14) D. W. Aksnes, S. M. Hutchison, and K. J. Packer, *Mol. Phys.*, **14**, 301 (1968).

(15) K. C. Moss, *J. Chem. Soc. A*, 1224 (1970).

The addition of water or 48% aqueous hydrofluoric acid to $AgSbF_6$ in acetonitrile showed similarly broadened lines. In the absence of information concerning possible exchange processes involving fluoride ion and viscosity and dielectric constant changes in these solutions, we are unable to account for the observed multiplet broadening.

### Experimental Section

**Sample Preparation.**—$AgSbF_6$ and $NaSbF_6$ were obtained from Alfa Inorganics and used without further purification. Spectro Grade solvents were used.

Solutions were normally prepared in the air although unnecessary exposure of reagents to the atmosphere was avoided. The possible effects of moisture absorbed from the atmosphere were tested by preparing a sample solution under dry nitrogen. Acetonitrile was dried by distillation from calcium hydride under nitrogen and a previously unopened sample of $AgSgF_6$ was recrystallized from this solvent. The $^{19}F$ nmr of this solution showed no significant difference compared to that of a similar solution prepared in the air with spectroscopic grade solvent.

On exposure to light, freshly prepared solutions of $AgSbF_6$ produced a black material, presumably metallic silver, after a few minutes. This did not appear to affect the nmr spectra in any way other than to decrease signal intensity after exposure to light for several days.

**Nmr Spectra.**—The $^{19}F$ spectra were obtained using a Varian HA-100 spectrometer operating at 94.1 MHz. The spectrum illustrated in Figure 1 was obtained using a modified HA field-sweep mode. The lock was switched off and the manual oscillator was replaced by an external oscillator generating about 15,000 Hz. We were unable to obtain a symmetrical intensity pattern using this mode. The coupling constants were determined by scanning each component separately in an HA frequency-sweep mode using trifluoroacetic acid to provide a lock signal Considerable difficulty was experienced in correctly phasing the broad (100–200 Hz) components in this mode. Consequently, each value was obtained from measurements on the two appropriate components with the best line shapes. The precision is a subjective estimate of the accuracy in determining the band maxima.

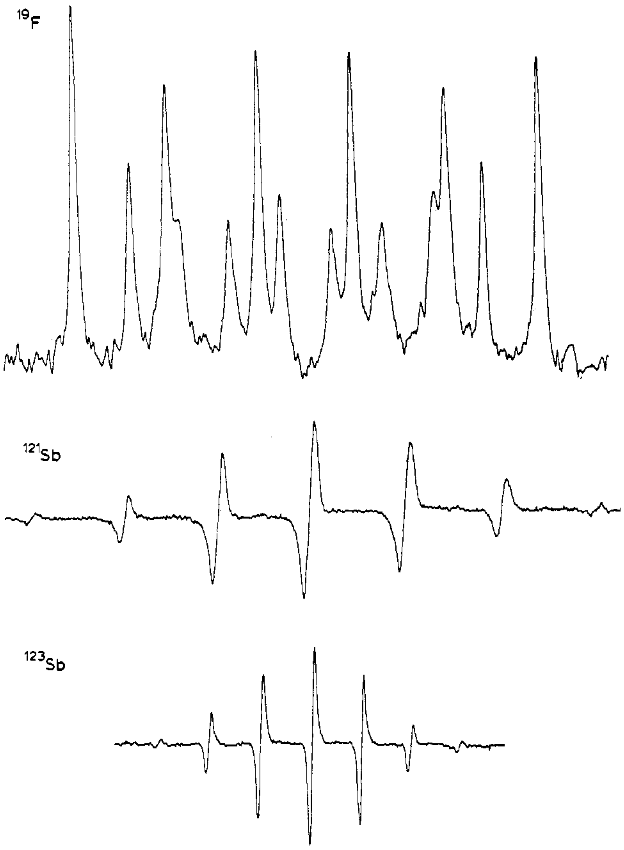

Figure 1—The $^{19}F$, $^{121}Sb$, and $^{123}Sb$ nmr spectra of the $SbF_6^-$ ion. The spectra are shown relative to a common frequency scale.

The $^{12}Sb$ and $^{123}Sb$ nmr spectra were obtained with a Varian 4200B wide-line spectrometer combined with a 9-in. magnet. In a field of 14.1 kG, frequencies of 14.4 and 7.8 MHz were used for $^{121}Sb$ and $^{123}Sb$, respectively. The spectra shown in Fgure 1 were recorded as the derivative of the absorption mode.

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CONTRIBUTION NO. 1867 FROM THE CENTRAL RESEARCH
DEPARTMENT, E. I. DU PONT DE NEMOURS AND COMPANY,
EXPERIMENTAL STATION, WILMINGTON, DELAWARE 19898

## Tellurates of the Type $A^{2+}TeO_4$

BY A. W. SLEIGHT,* C. M. FORIS, AND M. S. LICIS

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Although sulfates and selenates of the $A^{2+}SO_4$ and $A^{2+}SeO_4$ types are well known, little is known about anhydrous $A^{2+}TeO_4$ tellurates. Only $BaTeO_4$ is well established.[1,2] We have now prepared and characterized tellurates of this type where A is Mg, Ca, Sr, Ba, Cd, or Pb.

### Experimental Section

The reactants were reagent grade or better. The syntheses were generally carried out at high pressure and temperature. Appropriate quantities of the reactants were intimately mixed, sealed in gold tubes, and heated at 700° with 3000 atm of supporting pressure for 8 hr. The reactant mixtures were of the types $ACl_2 \cdot xH_2O$–$Na_2TeO_4 \cdot 2H_2O$, AO–$H_2TeO_4 \cdot 2H_2O$, or $A(OH)_2 \cdot xH_2O$–$H_2TeO_4 \cdot 2H_2O$. A mixture of $PbO_2$ and $TeO_2$ could also be used to prepare $PbTeO_4$. Preparations at 600° under 1 atm of flowing oxygen were successful for making polycrystalline samples of $BaTeO_4$, $SrTeO_4$, and $CdTeO_4$.

*Anal.* Calcd for $MgTeO_4$: Mg, 11.3; Te, 59.1; O, 29.6. Found: Mg, 11.5; Te, 58.7; O, 29.4. Calcd for $CdTeO_4$: Cd, 37.0; Te, 42.0; O, 21.0. Found: Cd, 36.8; Te, 42.3; O, 21.4. Calcd for $CaTeO_4$: Ca, 17.3; Te, 55.1; O, 27.6. Found: Ca, 17.2; Te, 55.4; O, 27.3. Calcd for $SrTeO_4$: Sr, 31.4; Te, 45.7; O, 22.9. Found: Sr, 31.4; Te, 45.5; O, 22.8. Calcd for $BaTeO_4$: Ba, 41.8; Te, 38.8; O, 19.5. Found: Ba, 41.9; Te, 38.4; O, 19.1. Calcd for $PbTeO_4$: Pb, 52.0; Te, 32.0; O, 16.0. Found: Pb, 52.4; Te, 29.9; O, 16.2.

X-Ray powder patterns were obtained on all products at 25° using a Guinier–Hägg camera with Cu $K\alpha_1$ radiation and an internal standard of KCl ($a$ = 6.2931 Å). Single-crystal photographs were taken with a precession camera using Mo radiation. Cell dimensions were refined by least squares using the Guinier data.

Thermogravimetric analyses (tga) employed a Du Pont 900 thermal analyzer and a heating rate of 10°/min.

### Results

The $A^{2+}TeO_4$ tellurates where $A^{2+}$ is Mg, Ca, Sr, Ba, or Cd are white, and $PbTeO_4$ is light yellow. They

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[1] A. Engelbrecht and F. Sladky, *Monatsh. Chem.*, **96**, 360 (1965).

[2] R. N. Knyazeva and A. P. Kurapova, *Russ. J. Inorg. Chem.*, **14**, 1220 (1969).