

Received May 8, 1979

SYNTHESES AND RAMAN SPECTRA OF NITROSYL FLUOROMETALLATE SALTS

W.A. SUNDER, ANDREA L. WAYDA⁺, DOREEN DISTEFANO, W.E. FALCONER

and J.E. GRIFFITHS^{*}

Bell Laboratories

Murray Hill, New Jersey, 07974

ABSTRACT

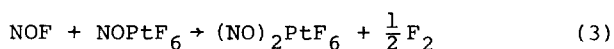
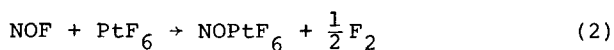
Nitrosyl salts containing MF_6^- , $MF_6^{=}$, MF_6^{\equiv} , MF_7^- and $MF_8^{=}$ (M = Cr, Mo, W, Re, Rh, Ru, Os, Ir, Pd, Pt and Ru) have been synthesized using $NOF + F_2$ or NO with the appropriate metal or metal fluoride as reactants. All of the compounds were characterized by their Raman spectra and each spectrum was analysed in terms of the fundamental vibrations of cations and anions. Analysis of the Raman spectra of the product formed in the reaction of $NOAuF_6$ with NOF and F_2 lead to the conclusion that $(NO)_2Au(IV)F_6$ is a reaction product.

* To whom correspondence should be addressed.

⁺ Present Address: University of Chicago, Chicago, Illinois 60637.

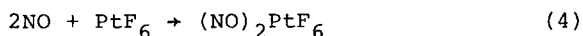
I. INTRODUCTION

A variety of nitrosyl fluorometallate salts have been synthesized by the interaction of nitrosyl fluoride with strongly oxidizing metal fluorides and with strong fluoride ion acceptors, as exemplified in the following equations [1-3]

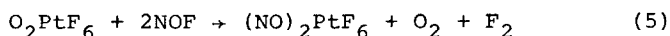


There are many examples of such reactions that could be listed [4-10], including those where the stable anions may be heptacoordinate, MF_7^- and $\text{MF}_7^{=}$, or octacoordinate, $\text{MF}_8^{=}$ and $\text{MF}_8^{=}$ [4,11-15]. Compounds of these types are often encountered as salts of the alkali metals [11-15].

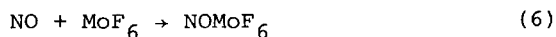
Dinitrosyl salts, $(\text{NO})_2\text{MF}_6$, have also been synthesized by oxidation of nitric oxide [1-3].



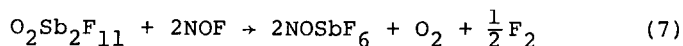
or by reactions of the type,



With the former, several complications can arise. If the oxidizing strength is too small, only the first stage of the reaction occurs [1-5], e.g.



while in some cases of high oxidizing power, reduction of the central metal atom proceeds to oxidation states less than four. Reaction (5) has also been useful for converting more complicated anions to structurally simpler forms [4],



It is evident that there are a number of syntheses available for producing fluorometallate salts with one, two, or three nitrosyl cations. When a metal can exist in several oxidation states, it is not always clear at the outset which of several possible reaction products will obtain, nor has it always been a trivial matter to characterize the products in a simple way. Where more than one salt may form, it is important to delineate the conditions which favor each of the possibilities so that, ideally, each compound may be isolated in a state of reasonable purity.

In the present work we have prepared a number of salts containing various combinations of NO^+ , MF_6^- , $\text{MF}_6^{=}$, MF_7^- , $\text{MF}_7^{=}$, MF_8^- and $\text{MF}_8^{=}$ ions using the synthetic routes outlined above. Temperature, time and the pressure of volatile reactants were used as variables. In addition, the reaction of elemental metals (Pd, Rh, Ru, Au and Ag) with NOF and F_2 in a one step process has been used successfully to prepare $(\text{NO})_2\text{PdF}_6$, $(\text{NO})_2\text{RhF}_6$, and NOAuF_4 . The method is not useful for all metals. Nevertheless, by employing the available synthetic routes and by a judicious selection of reaction conditions, fairly pure products could be obtained and each was characterized in terms of its Raman spectrum.

Spectroscopic observations are further useful in identifying reaction intermediates and products formed in more complicated reactions that occur under much more severe conditions. It is of value, therefore, to have spectra available of compounds containing a wide variety of fluorometallate anions with a common cation.

The nitrosyl salts were selected because the frequency and band contours of the Raman band corresponding to the NO^+ stretching fundamental can give useful supplementary information about the nature of the anion and the oxidation state of the central metal atom therein [1,4]. This type of corroborative evidence is not available with the alkali metal salts.

For several compounds, Raman spectra had already been reported and were well understood. For others, spectra were available only for samples of questionable authenticity. In a few cases, the spectra themselves were poorly understood. In the present work, new spectral data are presented, the preparations and Raman spectra of some new compounds are reported and a compilation of data for a large number of related species is given. Finally, evidence for the new compound, $(\text{NO})_2\text{AuF}_6$, is offered even though the material could not be isolated from the other reaction products, NOAuF_6 and NOAuF_4 . The compound is of special interest because no compound of gold in a +4 oxidation state has been characterized before.

II. EXPERIMENTAL SECTION

All reactions were done in openable Monel reactors [1,3]. Volatile reactants and products were transferred to and from the reactor via a Monel vacuum line and pressures were measured with nickel Bourdon gauges. Involatile materials were handled in a helium filled controlled atmosphere box (combined water and oxygen content <1 ppm). Products were stored therein in Teflon bottles.

A rotatable Raman cell of Monel fitted with a sapphire window was used [4]. Excitation for Raman spectral studies was accomplished with the 5145 and 6471 Å lines of Spectra Physics argon and krypton lasers as required. Raman spectra were recorded with an Instruments S. A. Ramanor HG-2S instrument equipped with a photon count rate detection system (SSR 1105).

A number of metal fluorides, NbF_5 , TaF_5 , ReF_6 , RuF_5 , OsF_6 , RhF_5 , RhF_6 , IrF_6 , PtF_5 , PtF_6 and AuF_3 , were synthesized using known methods [16]. WF_6 was purchased from Varlacoid Chemical Co. and was purified by low temperature distillation. MoF_6 was purchased from Allied Chemical Co. and was not purified further. Several dioxygenyl salts were made using literature methods [1,16-19].

Nitrosyl fluoride was from Ozark-Mahoning Co., and analysed mass spectroscopically to be >99%. It was used without purification.

Gas-solid reactions. All reactions between solid materials such as Rh, AuF_3 , O_2AuF_6 , NOWF_7 and TaF_5 and the volatile materials NO, NOF and F_2 were done in the same way.

In a typical reaction, 6.4 mmole of palladium powder and a mixture of molecular fluorine and nitrosyl fluoride ($F_2:NOF = 3.5:1$) at a total pressure of 4.5 atmospheres were heated in a Monel reactor (260 cm^3) at 300°C for 51 hours. After removal of excess NOF and F_2 , a pale yellow product was identified by its Raman spectrum as $(NO)_2PdF_6$ [20]. No evidence for unreacted palladium was found. Similar reactions with rhodium and gold yield $(NO)_2RhF_6$ and $NOAuF_4$ respectively. This procedure did not yield $NORhF_6$ and $NOAuF_6$ (vide infra). With silver, AgF_2 is the major product and with ruthenium, $NORuF_6$ is the predominant compound formed.

The preparations of $(NO)_2RhF_6$ and $NORhF_6$ without mutual contamination are best accomplished using O_2RhF_6 as starting material. From the reaction of O_2RhF_6 with a large excess of NOF at moderate temperatures ($\sim 50^\circ\text{C}$, 17 hr.), only $(NO)_2RhF_6$ is isolated. If a large excess of fluorine is used and the ratio of NOF : O_2RhF_6 is kept low ($\sim 2:1$), only the single salt $NORhF_6$ can be detected. The latter can also be made from the direct oxidation of NO with RhF_6 (vide infra). Other gas-solid reactions and a listing of products are summarized in Table I.

Gas-gas reactions. All reactions of the hexafluorides PtF_6 , IrF_6 , MoF_6 , WF_6 , ReF_6 , RuF_6 , RhF_6 , and OsF_6 plus the volatile pentafluorides of P, As, and Sb with NOF, NOF + F_2 and NO were done in the same way. Reactants were measured (P,V,T) and condensed in a Monel reactor. After reaction at some suitable temperature, volatile materials were pumped away or were collected and measured. Solid products were removed from the reactor in the dry box.

In a typical reaction, about 1.0 mmole of MoF_6 and a large excess of NOF were allowed to react overnight at room temperature. After removal of excess reactants, a white solid product was identified by its Raman spectrum as NOMoF_7 slightly contaminated with $(\text{NO})_2\text{MoF}_8$. If the reaction occurs with excess MoF_6 , only the NOMoF_7 product is recovered. When the reactants are NO and MoF_6 , the product is NOMoF_6 . A summary of results is contained in Table I.

Table I Summary of Reaction Products

Fluoride	Reactant ^a	Product	T(°C)	Time (hr)
CrF_5	$(\text{NOF})_x$	$(\text{NO})_2\text{CrF}_6$	25	17
	$(\text{NOF})_x$	$(\text{NO})_3\text{CrF}_6$	25	17
MoF_6	$(\text{NOF})_x$	NOMoF_7	25	66
$(\text{MoF}_6)_x$	NOF	NOMoF_7	25	1.5
MoF_6	NO	NOMoF_6	25	17
WF_6	$(\text{NOF})_x$	NOWF_7	50	17
		$(\text{NO})_2\text{WF}_8$		
$(\text{WF}_6)_x$	NOF	NOWF_7	25	15
NOWF_7	$(\text{NOF})_x$	$(\text{NO})_2\text{WF}_8$	53	66
ReF_6	NO	NOREF_6	50	17
Ru	$(\text{NOF}+\text{F}_2)_x$	NORuF_6	300	21
RuF_6	$(\text{NOF})_x$	NORuF_6	25	21
RuF_6	NO	NORuF_6	25	21
NORuF_6	$(\text{NOF})_x$	$(\text{NO})_2\text{RuF}_6$	150	42
O_2RuF_6	$(\text{NOF})_x$	NORuF_6	25	15

(continued on following page)

Table I (cont.)

Fluoride	Reactant ^a	Product	T(°C)	Time (hr)
OsF ₆	NO	NOOsF ₆	50	19
OsF ₆	(NOF) _x	NOOsF ₆	50	17
Rh	(NOF+F ₂) _x	(NO) ₂ RhF ₆	300	15
RhF ₆	(NOF+F ₂) _x	NORhF ₆	25	1
RhF ₆	(NOF) _x	(NO) ₂ RhF ₆	25	19
O ₂ RhF ₆	(NOF) _x	(NO) ₂ RhF ₆	100	11
IrF ₆	NOF + F ₂	NOIrF ₆	25	4
IrF ₆	(NOF) _x	NOIrF ₆	25	4
		(NO) ₂ IrF ₆		
Pd	(NOF+F ₂) _x	(NO) ₂ PdF ₆	300	62
PtF ₅	NOF	NOPtF ₆	25	17
PtF ₆	(NOF) _x	(NO) ₂ PtF ₆	25	17
PtF ₆	(NOF+F ₂) _x	NOPtF ₆	25	12
NOPtF ₆	NOF	(NO) ₂ PtF ₆	100	17
O ₂ PtF ₆	NOF	(NO) ₂ PtF ₆	100	16
O ₂ AuF ₆	(NOF) _x	NOAuF ₆	150	17
Au	(NOF+F ₂) _x	NOAuF ₄	230	64
O ₂ AuF ₆	(NOF+F ₂) _x	NOAuF ₆	82-100	172
		(NO) ₂ AuF ₆		
		NOAuF ₄		

a. x = large excess.

III. RESULTS AND DISCUSSION

The anions formed in the reactions to be discussed include $M(V)F_6^-$, $M(IV)F_6^{=}$ and $M(III)F_6^{=}$, $M(VI)F_7^-$, $M(V)F_7^{=}$ and $M(VI)F_8^{=}$. Data for the octahedral species $M(V)F_6^-$, $M(IV)F_6^{=}$ and $M(III)F_6^{=}$ are collected in Tables II and III. Vibrational frequencies for the more complicated heptacoordinate and octacoordinate anions are summarized in Table IV. The corresponding frequencies for the stretching fundamentals of the NO^+ cations also appear in these tables.

Representative spectra for $NORhF_6$, $(NO)_2RhF_6$, $NOAuF_6$, a mixture of $NOAuF_6$, $(NO)_2AuF_6$ and $NOAuF_4$ and $NOWF_7$ and $(NO)_2WF_8$, are given in Figures 1-4. A correlation diagram of the fundamentals of IrF_6^- , PtF_6^- , AuF_6^- , $IrF_6^{=}$, $PtF_6^{=}$ and $AuF_6^{=}$ is presented in Figure 5. The latter is important for subsequent discussion of the unusual characteristics of the spectra of the two fluoroaurate species $Au(V)F_6^-$ [21] and $Au(IV)F_6^{=}$.

Raman Spectra of Hexacoordinate Anions. Spectra of most of the hexacoordinate species are quite straightforward. The anion spectra consist of three Raman bands; the highest frequency band is normally the most intense and has the narrowest line width. It is the non-degenerate symmetric stretching mode and is labelled ν_1 (a_{1g}). The degenerate bands ν_2 (e_g) and ν_5 (f_{2g}), in many cases, are split reflecting a lowering of the side group symmetry. Interesting exceptions are the fluoride species containing the $Au(IV)$ and $Au(V)$ central atoms; these will be discussed later.

Table II Vibrational Spectra of MF_6^- Anions

Compound	Fundamental Frequencies (cm^{-1})				Refs.		
	$\nu_1(a_{1g})$	$\nu_2(e_g)$	$\nu_5(f_{2g})$	$\nu(\text{NO}^+)$			
NONbF_6	686	584	291	2340	4		
		554	273				
NOTaF_6	697	575	277	2339	4		
NOMoF_6	688	-	236	2330	b		
	(688)	(450)	(236)	-	5		
NOWF_6	706	-	215	-	b		
	(707)	(407)	(215)	-	5		
NOReF_6	697	[622] ^a	249	2330	b		
		[591] ^a					
		(703)	(449)	(249)		-	5
NORuF_6	660.3	600	277	2330	b		
		578	266				
			254				
NOOsF_6	688	623	261	2334	b		
		605	247	-			
		(691)	(624)	(262)		-	5
NORhF_6	632	554	262	2328	b		
			248				
NOIrF_6	671	588	256	2334	.1		
		564	244				
		563	230				
		(667)	550	250		-	5
		450					
O_2PdF_6	643	570	268	-	25,26		

(continued on facing page)

Table II (cont.)

Compound	Fundamental Frequencies (cm ⁻¹)				Refs.
	$\nu_1(a_{1g})$	$\nu_2(e_g)$	$\nu_5(f_{2g})$	$\nu(NO^+)$	
NOPtF ₆	643	590	249	2332	1, 3, 7
		574	237		
			224		
NOAuF ₆	598.3	594.7	229	2326	21
			219		
NOPF ₆	746	575	477	2339	4
NOAsF ₆	688	575	375	2339	4
NOSbF ₆	657	594	295	2342	4
		568	285		
NOBiF ₆	588	549	249	2339	4
		522	234		
			217		

a. Assignment tentative.

b. This work.

Table III Vibrational Spectra of MF₆⁼ Anions

Compound	Vibrational Frequencies (cm ⁻¹)				Refs.
	$\nu_1(a_{1g})$	$\nu_2(e_{2g})$	$\nu_5(f_{2g})$	$\nu(NO^+)$	
(NO) ₂ RuF ₆	609	-	236	2311	a
(NO) ₂ RhF ₆	592	500	242	2312	a
		480			
(NO) ₂ PdF ₆	573	554	246	2312	a, 20
(NO) ₂ IrF ₆	610	528	219	2315	1
(NO) ₂ PtF ₆	597	572	218	2316	1
(NO) ₂ AuF ₆	595	593	220	2312	a
(NO) ₂ CrF ₆	610	-	298	2312	a

a. This work.

Table IV Vibrational Spectra of MF₇ and MF₈

 MF₇⁻ and MF₇⁼ Species

$$C_{2v} \quad \Gamma = 6A_1(R,IR) + 3A_2(R) + 5B_1(R,IR) + 4B_2(R,IR)$$

$$D_{5h} \quad \Gamma = 2A_1'(R) + 2A_2''(IR) + 3E_1'(IR) + 2E_2'(R) + E_1''(R)$$

 MF₈⁼ Species

$$D_{4d} \quad \Gamma = 2A_1(R) + 2B_2(IR) + 3E_1(IR) + 3E_2(R) + 2E_3(R)$$

NOMoF ₇	NOWF ₇	(NO) ₂ NbF ₇ ^a	(NO) ₂ TaF ₇ ^a	(NO) ₂ WF ₈
689	715	634	634	660
630	693	-	(590)	611
510	595	388	450	489
421	440	315	390	418
(330)	-	-	-	390
306	329	257	303	357 327

ν(NO ⁺)				
2329.9	2330	-	-	-
		-	-	-
2325.4	2326			
-	-	2322	2324	2324

a. See also ref. 4.

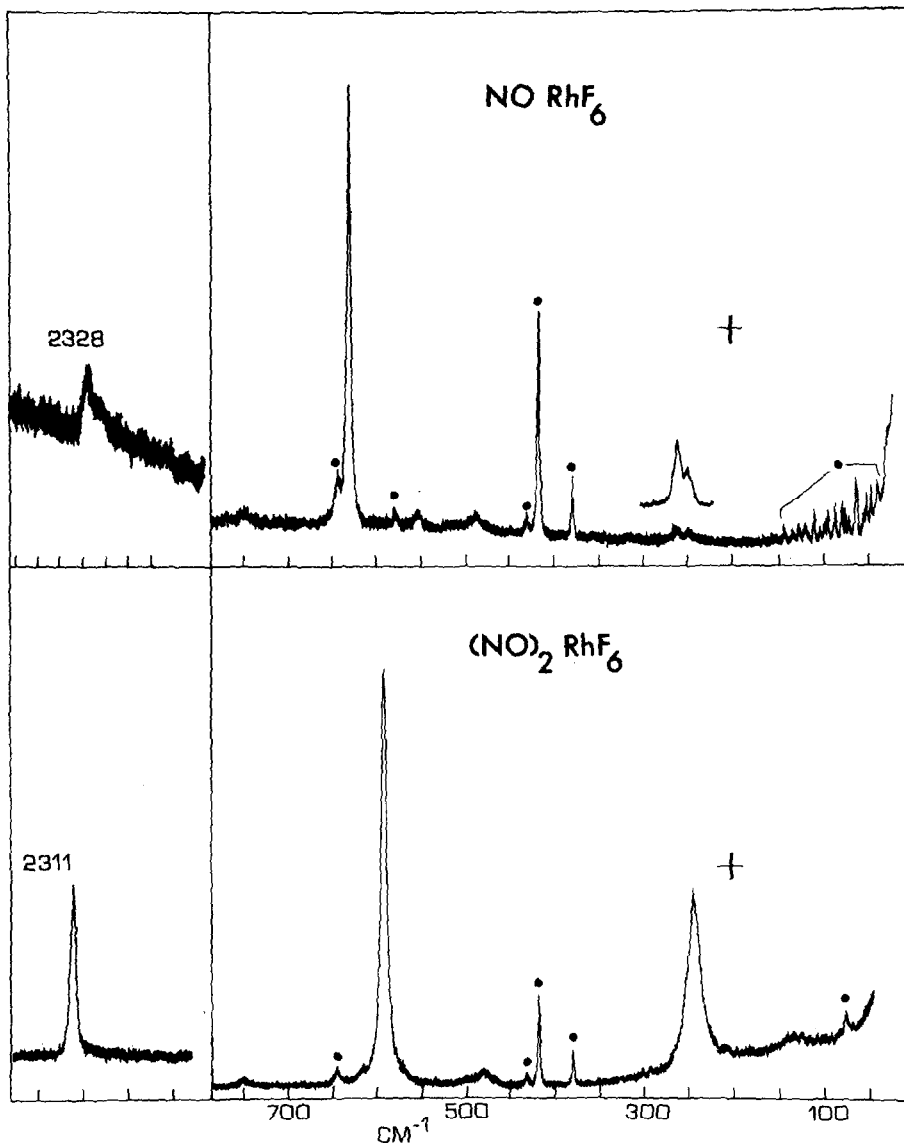


Fig. 1 Raman spectra of NO RhF_6 (top) and $(\text{NO})_2 \text{RhF}_6$ (bottom). Laser power (5145 \AA) 1.1 W, scan rates $50 \text{ cm}^{-1}/\text{min}$, spectral slit width 2 cm^{-1} , sensitivity (top) 10^4 c/s(FS) , (bottom) $3 \times 10^4 \text{ c/s(FS)}$, time constant 0.1 sec. Dots • denote laser plasma lines or Raman lines due to air at low frequencies.

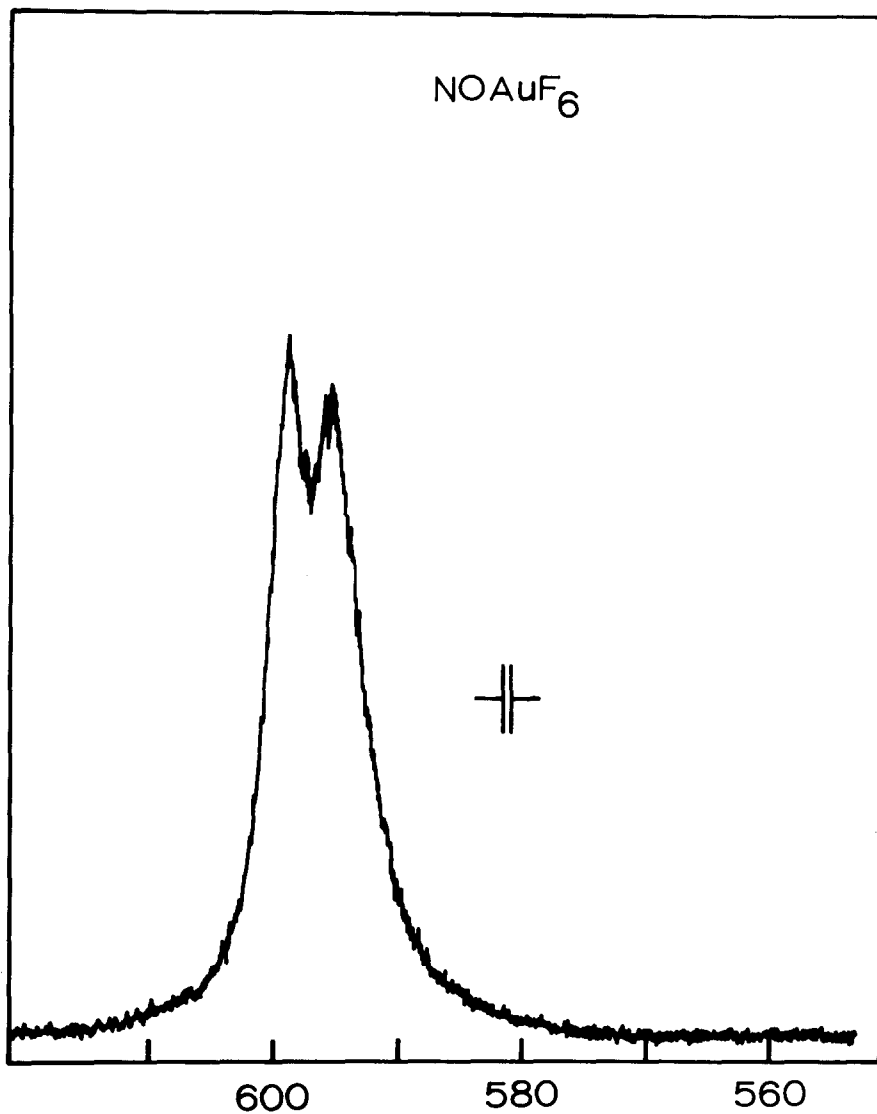


Fig. 2 Raman spectrum of ν_1 and ν_2 of the AuF_6^- anion. Scan rate $5 \text{ cm}^{-1}/\text{min}$, spectral slit width 0.6 cm^{-1} , laser power (5145 \AA) 1.0 W , sensitivity 10^4 c/s(FS) , time constant 0.1 sec .

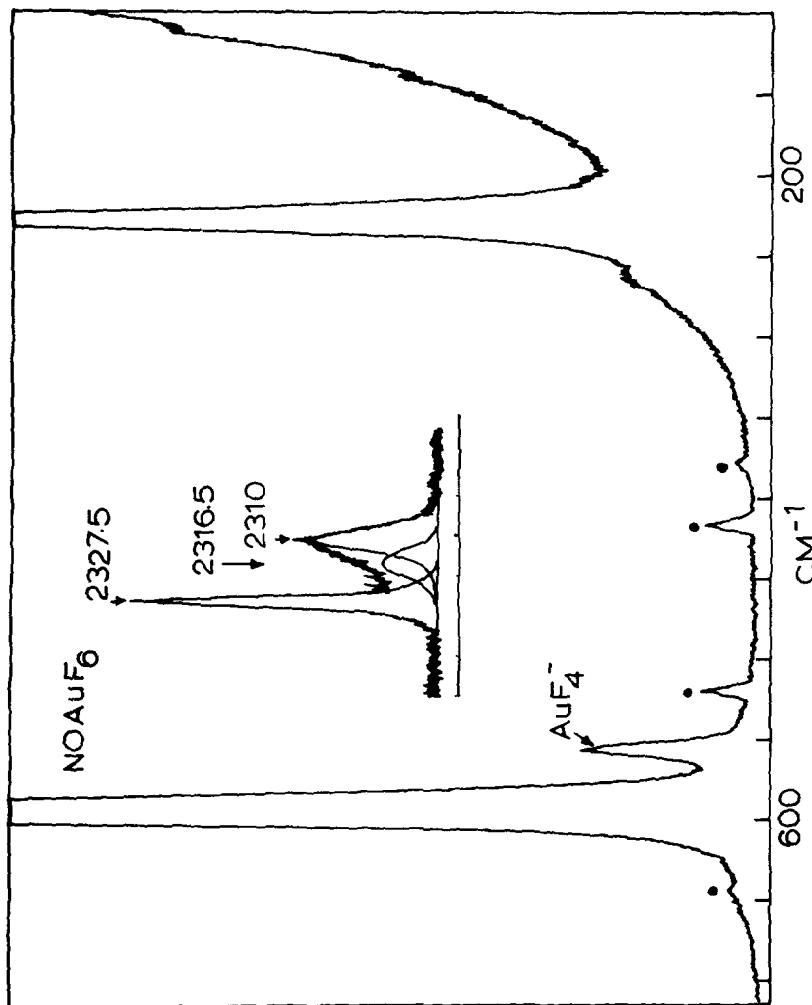


Fig. 3 Raman spectrum of NOAuF_6 , $(\text{NO})_2\text{AuF}_6$ and NOAuF_4 reaction product mixture. Laser power (5145 \AA) 1.0 W, scan rate $50 \text{ cm}^{-1}/\text{min}$, spectral slit width 5 cm^{-1} , sensitivity $3 \times 10^4 \text{ c/s(FS)}$, time constant 0.1 sec.

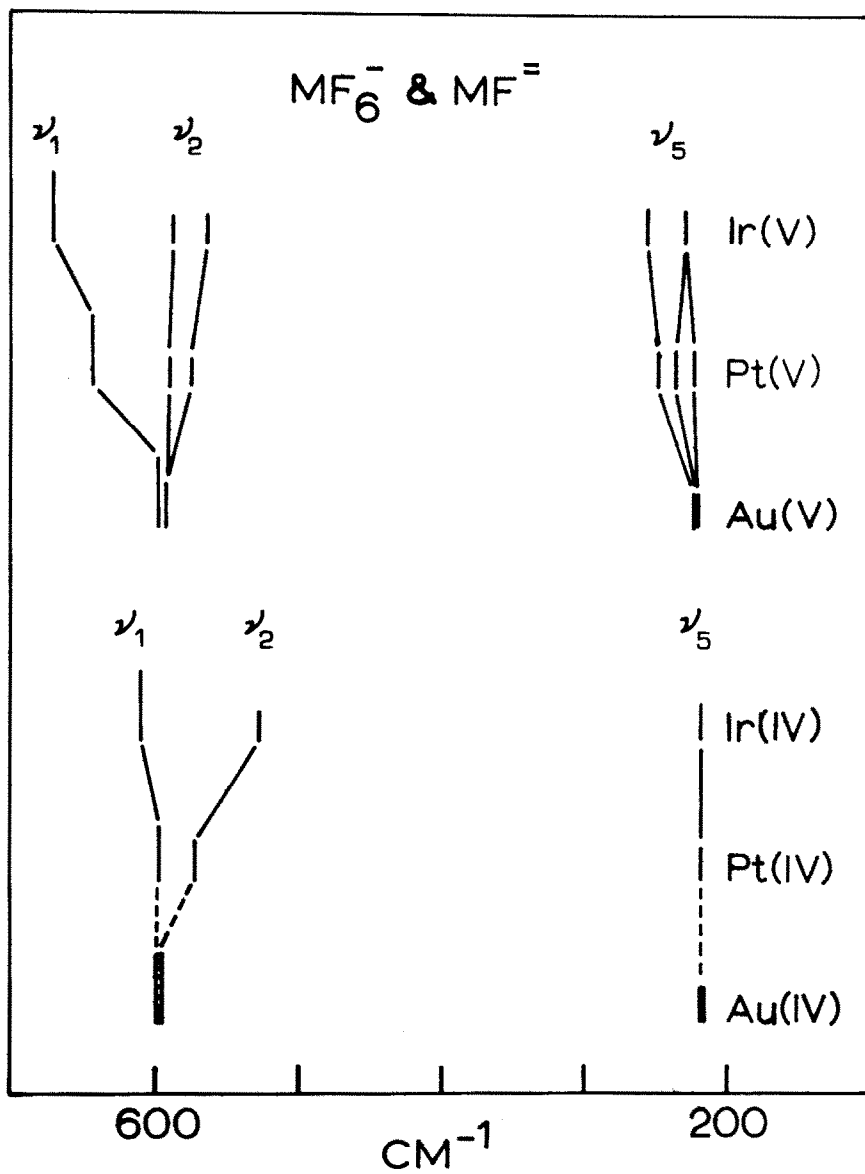


Fig. 4 Correlation diagram of fundamentals of MF_6^- and MF_6^{2-} anions.

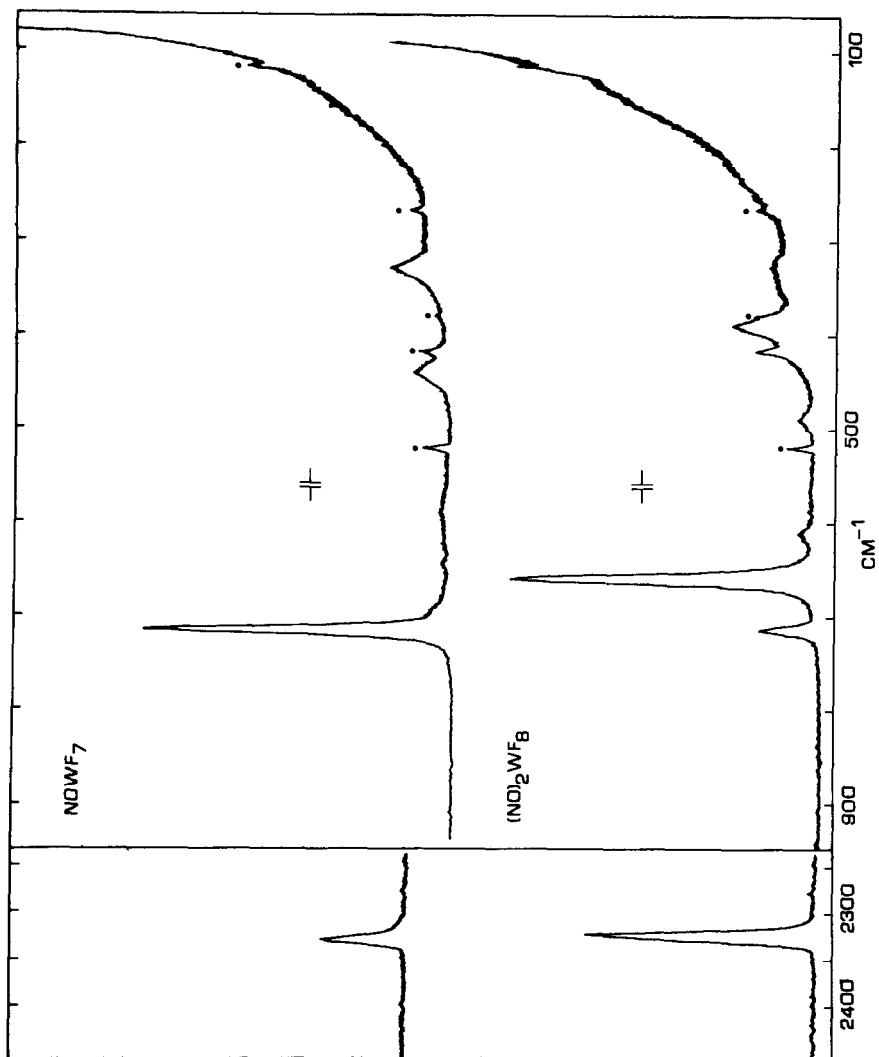


Fig. 5 Raman spectra of NOWF_7 (top) and $(\text{NO})_2\text{WFB}$. Experimental variables are the same as in Fig. 1 (bottom).

The basic features of all of the spectra of the compounds studied are as outlined above. Thus there is no doubt that octahedral coordination occurs. The basic trends in the frequencies of ν_1 have been discussed before [1,5,12]. They range from 746 cm^{-1} (PF_5^-) to 588 cm^{-1} (BiF_6^-) among the anions containing main group elements and from 706 cm^{-1} (WF_6^-) to 598 cm^{-1} (AuF_6^-) among those containing transition metals as the central atom. The ν_1 frequencies are greater for those anions containing the central atom in a higher oxidation state, e.g. ν_1 (Pt(V)F_6^-) = 643 cm^{-1} , ν_1 (Pt(IV)F_6^{2-}) = 595 cm^{-1} . The ν_5 fundamentals and to a lesser extent the ν_2 modes show similar but less pronounced sensitivity to the mass and oxidation state variables.

Raman Spectra of Heptacoordinate Anions. Structures of MF_7 species are expected to be monocapped trigonal prisms (C_{2v} point group) or pentagonal bipyramids (D_{5h} point group) regardless of whether the species are neutral molecules like IF_7 , singly charged anions such as MoF_7^- , or doubly charged ions like NbF_7^{2-} . The selection rules are significantly different for the two structures (Table III) in that 18 Raman bands for C_{2v} and 5 Raman bands for D_{5h} should obtain. The spatial configurations of these two structures, however, are quite similar and at ordinary temperatures the energy barrier between them may be quite small. It is likely, therefore, that a dynamic interconversion between the two occurs [23]. In that event, the observed spectrum would most likely resemble that of the more symmetric possibility. The conclusions, therefore, may be ambiguous. Alternatively, a phase change, $\text{D}_{5h} \leftrightarrow \text{C}_{2v}$, may occur at lower temperatures during which more profound spectral changes may occur.

There is no clear way to predict the temperature at which such transitions occur. Recent results at 298 and 77 K demonstrate clearly the types of spectral changes that can occur with decreasing temperature for systems such as NOUF_7 [11].

Data obtained for NOMoF_7 , NOWF_7 , $(\text{NO})_2\text{NbF}_7$ and $(\text{NO})_2\text{TaF}_7$ have common general features. The basic spectra consist of five Raman bands and only one of these is narrow and intense. In the spectrum of NOMoF_7 , a sixth band can be inferred from an asymmetry in the band contour of the lowest frequency band whose center is near 306 cm^{-1} . The strongest band in all of the spectra, however, undoubtedly represents a totally symmetric stretching fundamental of the A_1' species (D_{5h}). Detailed assignments of the remaining bands to specific symmetry or normal coordinates is unwarranted without further information. Two problems do arise, however, when the complete spectra of all of the compounds of this general type are considered. The band at 693 cm^{-1} in the spectrum of NOWF_7 is very weak and ill-defined. It was expected to occur at about 650 to 660 cm^{-1} . The corresponding band in the spectrum of $(\text{NO})_2\text{NbF}_7$ was not observed at all. Despite these ambiguities, the observed spectra are most consistent with pentagonal bipyramidal structures. Our results and conclusions, with only minor differences, are similar to those reported recently in studies of related salts of the alkali metals. The question for which we do not have supportable evidence, however, is whether a facile interconversion of the $D_{5h} \leftrightarrow C_{2v}$ occurs at room temperature or not [23].

Raman Spectra of Octacoordinate Species. The only octacoordinate species isolated in reasonably pure form was $(\text{NO})_2\text{WF}_8$ and the observed spectrum (Fig. 5 and Table IV) was completely in accord with that expected for a square anti-prism structure. Seven well defined Raman bands were observed, four more than were reported for the analogous alkali metal salts [15]. As in the case of the heptacoordinate species, further analysis in terms of symmetry or normal coordinates is not justified. The conclusion concerning the square anti-prism structure, however, is in accord with that of Beuter et al. on similar compounds, K_2WF_8 , Rb_2WF_8 and Cs_2WF_8 [15].

Cation Spectra, NO^+ , $(\text{NO}^+)_2$ and $(\text{NO}^+)_3$. In earlier work [1,4], in which the Raman spectra of several nitrosyl complexes were analyzed, it was suggested that the frequency and band contour of the Raman bands resulting from the NO^+ stretching mode could be used to determine the number of NO^+ ions per formula unit. Thus additional information about the nature of the anion and the oxidation state of the central metal atom therein was available. In all of the salts studied thus far, the NO^+ stretching frequency for compounds containing a single NO^+ cation (NOMF_6 and NOMF_7) occur in a narrow spectral range 2326-2342 cm^{-1} . The various frequencies as a function of the central metal atom are given in Tables II-IV.

Salts containing two NO^+ cations per formula unit have their NO^+ stretching frequencies in a slightly lower range 2311-2324 cm^{-1} . The frequencies are at the upper end of this range when the anions involve Nb, Ta and W and have structures of lower symmetry than O_h . When the MF_6 anionic species is a strong oxidizing agent ($\text{M} = \text{Ru}, \text{Rh}, \text{Pd}, \text{Pt}, \text{Ir}$ and Au)

rather than a strong fluoride ion acceptor and the anion has a basic octahedral structure (Table III); the frequencies of the NO^+ stretching modes occur in a very narrow range indeed (2311 to 2315 cm^{-1}). The band contours for these compounds having two NO^+ units are also somewhat wider than for compounds containing only a single NO^+ cation. Therefore, even in cases where the anion spectra are not of the highest quality, and this occurred for $(\text{NO})_2\text{RuF}_6$ and $(\text{NO})_2\text{IrF}_6$, it is a simple matter to identify the reaction product from the cation spectrum. These characteristic features are also useful when contamination of the product is suspected. For example, small amounts of $(\text{NO})_2\text{WF}_8$ generally form in addition to the major product NOWF_7 in the reaction of NOF with WF_6 . Interpretation of the cation properties outlined above prevents us from assigning an extra band or bands in the anion spectra to a structural perturbation.

The only salt in this study containing three NO^+ cations per formula unit is $(\text{NO}^+)_3\text{CrF}_6^{3-}$. In this case the band contour of the NO^+ stretching mode is at least twice that of the one for the $(\text{NO})_2\text{CrF}_6$ compound. The band center is at 2290 cm^{-1} , considerably lower than the value of 2312 cm^{-1} observed for $(\text{NO})_2\text{CrF}_6$. In general, therefore, the NO^+ stretching frequencies decrease and the band widths of the NO^+ fundamentals increase as the oxidation state of a given central metal atom in the anion decreases.

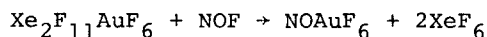
There is one exception to this general rule and it is found in the spectrum of NOAu(III)F_4 . The NO^+ stretching frequency at 2310 cm^{-1} is much lower [8] than for other compounds containing a single NO^+ cation (c.f. Table II). The

low frequency, however, is quite consistent with that expected for a salt with an anion containing a central metal atom in a low oxidation state (+3). The band contour in $\text{NO}^+\text{AuF}_4^-$ is narrow as expected for a salt containing only a single NO^+ ion.

The overall conclusions, therefore, are that the number of NO^+ cations per formula unit dominates the shape of the band contour. The oxidation state of the central atom in the anion as well as the number of NO^+ ions per formula unit determines the frequencies at which the NO^+ fundamentals occur. These rules, or observations, complement information obtained from anion spectra and allow more definitive conclusions to be reached about the products formed in reactions of the type presented in this work.

Hexafluoroaurate (IV) Anion. In numerous compounds of gold, the +1, +3 and +5 states are quite stable. In principle compounds of gold in +4 and +6 oxidation states should also exist. Bartlett has studied various ways to produce compounds of Au(IV) in detail [8] and has advanced reasons why the AuF_6^- anion is expected to be unstable with respect to further reduction from the +5 state to +3. Furthermore, it was proposed [8] that a fluoroaurate of Au(IV), if it were to exist as a stable identifiable entity, would surely exist as the AuF_5^- anion. These speculations prompted us to try to prepare a compound of Au(IV), either $(\text{NO})_2\text{AuF}_6$ or NOAuF_5 , neither of which had been characterized previously.

Earlier work by Bartlett and Leary [8] demonstrated that



was a suitable reaction for the preparation of pure NOAuF_6 . The subsequent reaction of this compound with NO resulted in the formation of NOAuF_4 , AuF_3 and metallic gold. It was necessary, in our view, to utilize a high pressure of excess fluorine along with a nominal excess of NOF in a reaction with NOAuF_6 so as to favor the production of $(\text{NO})_2\text{AuF}_6$ and to inhibit the reduction of gold to the +3 state. The reaction temperatures were varied between 25 and 100°C with the F_2 : NOF ratio equal to at least 5 and the total pressure at least 3 atmospheres. After removal of excess volatile materials, the solid product was a light yellow color (NOAuF_6 and NOAuF_4 are an almost white pale yellow color when pure).

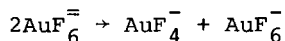
The anion spectrum (Fig. 3) can be accounted for in terms of the spectra of the AuF_6^- and the AuF_4^- anions. The cation spectra, on the other hand, cannot. In addition to the bands due to the NO^+ in NOAuF_6 at 2327.5 cm^{-1} and the NO^+ in NOAuF_4 at 2310 cm^{-1} , there is additional intensity due to a band less intense than either at 2316 cm^{-1} . The bands at 2327.5 and at 2310 cm^{-1} are known to have symmetric contours in the spectra of the pure materials. In view of our other studies on a variety of compounds containing one, two and three NO^+ ions per formula unit, one is led to the conclusion that a compound of the formula $(\text{NO})_2\text{AuF}_6$ exists in the reaction product mixture. One must ask, however, why the spectrum of the Au(IV)F_6^- species is undetectable at lower frequencies.

The answer involves a number of very unusual coincidences, the details of which become apparent upon considering the frequency and intensity trends among the fundamental modes of vibration in IrF_6^- , PtF_6^- , AuF_6^- , $\text{IrF}_6^{=}$, $\text{PtF}_6^{=}$ and $\text{AuF}_6^{=}$. The first three involving the +5 oxidation state and the last three involving the +4 oxidation state will be called A and B species respectively. The frequency trends in both series are shown in Figure 4 in the form of a correlation diagram. In each series, ν_1 decreases with increasing mass of the central metal atom and at the same time the average value of ν_2 increases. Simultaneously, the absolute splitting (cm^{-1}) between the components of ν_2 and the separation of $|\nu_1 - \nu_2|$ approaches zero in both series. There is a modest decrease in ν_5 in series A and an almost constant value in series B.

In addition to the frequency trends (Fig. 4), it is worthwhile to recall [1] that the intensity ratio for $\nu_1(\text{PtF}_6^-)/\nu_1(\text{PtF}_6^{=})$ was at least 2 and the same appeared to be true for the analogous iridium compounds. The corresponding ratios for $\nu_2(\text{PtF}_6^-)/\nu_2(\text{PtF}_6^{=})$ were very small [1]. Thus the situation with respect to the $\text{AuF}_6^{=}$ species is that all three fundamentals are expected to be masked by the spectrum of the dominant AuF_6^- anion.

The evidence for the existence of $(\text{NO})_2\text{AuF}_6$ is persuasive but lacks absolute conviction. Chemical analyses are not sufficiently accurate to be definitive either. Powder x-ray crystallography revealed the presence of NOAuF_6 [8], NOAuF_4 [25] and six unidentified lines of a

compound apparently isomorphous with $(\text{NO})_2\text{PtF}_6$. Clearly this is inadequate to identify positively $(\text{NO})_2\text{AuF}_6$ but it does offer support to the Raman analysis. AuF_3 and Au were not present in the product mixture. The possibility that NOAuF_5 may be among the products was considered but is incompatible with the Raman evidence. First, the band contour of the NO^+ fundamental for such a compound was expected to be sharper than the one observed and the anion spectrum was not expected to coincide accidentally with that of the AuF_6^- species. Accordingly, we conclude that $(\text{NO})_2\text{AuF}_6$ does exist although the tendency toward disproportionation,



as suggested earlier [8], is strong. We have not found any evidence for the existence of the $\text{Au}(\text{IV})\text{F}_5^-$ species, however.

ACKNOWLEDGMENTS

We are indebted to M. J. Vasile and F. A. Stevie for the mass spectral analysis of NOF and A. J. Edwards for some preliminary work with the synthesis of CrF_5 , $(\text{NO})_2\text{CrF}_6$ and $(\text{NO})_3\text{CrF}_6$. We also are grateful to N. Bartlett for transmitting information on his work with gold compounds prior to publication.

REFERENCES

- 1 J. E. Griffiths and W. A. Sunder, J. Fluor. Chem. **6**, 533 (1975).
- 2 N. Bartlett and S. P. Beaton, Chem. Comm., 167 (1966).
- 3 F. P. Gortsema and R. H. Toeniskoetter, Inorg. Chem. **5**, 1217 (1966).

- 4 J. E. Griffiths, W. A. Sunder and W. E. Falconer, Spectrochim. Acta, 31A, 1207 (1975).
- 5 J. Shamir and J. G. Malm, J. Inorg. Nucl. Chem. Supplement, 107 (1976).
- 6 L. Stein and F. A. Hohorst, J. Inorg. Nucl. Chem. Supplement, 73 (1976).
- 7 F. O. Sladky, P. A. Bulliner and N. Bartlett, J. Chem. Soc. (A) 2179 (1969).
- 8 N. Bartlett and K. Leary, Rev. Chim. Minerale, 13, 82 (1976).
- 9 N. Bartlett, S. P. Beaton and N. K. Jha, Chem. Comm. 169 (1966).
- 10 W. Kuhlman and W. Sawodny, J. Fluor. Chem. 9, 341 (1977).
- 11 R. Bougon, R. M. Costes, J. P. Desmoulin, J. Michel and J. L. Person, J. Inorg. Nucl. Chem. Supplement, 99 (1976)
- 12 O. L. Keller and A. Chetham-Strode, Jr., Inorg. Chem. 5, 362 (1966).
- 13 N. A. Matwiyoff, L. B. Asprey and W. A. Wageman, Inorg. Chem. 9, 2014 (1970).
- 14 O. L. Keller, Inorg. Chem. 2, 783 (1963).
- 15 A. Benter, W. Kuhlman and W. Sawodny, J. Fluor. Chem. 6, 367 (1975).
- 16 A. J. Edwards, W. E. Falconer, J. E. Griffiths, W. A. Sunder and M. J. Vasile, J. Chem. Soc. (Dalton) 1129 (1974) and references cited therein.
- 17 N. Bartlett and D. H. Lohmann, Proc. Chem. Soc. 115 (1962).
- 18 J. Shamir and J. Binenboym, Inorg. Chem. 2, 37 (1968).
- 19 J. B. Beal, C. Pupp and W. E. White, Inorg. Chem. 8, 828 (1969).

- 20 K. M. Leary, Ph.D. Thesis, University of California (Berkeley) May, 1975, p. 10 (LBL-3746).
- 21 J. E. Griffiths and W. A. Sunder, Spectrochim. Acta (in press).
- 22 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd. edit., J. Wiley and Sons, New York, 1978 and references cited therein.
- 23 L. B. Bernstein and K. S. Pitzer, J. Chem. Phys. **62**, 2530 (1975).
- 24 N. Bartlett, personal communication.
- 25 W. E. Falconer, F. J. DiSalvo, A. J. Edwards, J. E. Gfiffiths W. A. Sunder and M. J. Vasile, J. Inorg. Nucl. Chem. Supplement, 59 (1976).
- 26 V. P. Sokolov, Yu. V. Drobyshevskii, V. N. Prusakov, A. V. Ryzhkov and S. S. Khoroshev, Dokl. Akad. Nank. SSSR **229**, 641 (1976).