To the Graduate Council:

I am submitting herewith a dissertation written by William Harvey McCulla entitled "The Polytopicity of Ionic Ternary Compounds." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

Geo. K. Schweitzer
George K. Schweitzer, Major Professor

We have read this dissertation
and recommend its acceptance:

F. A. Grimm

C. Woods

Fred M. Stoops

Accepted for the Council:

L. Edwards Poth
Vice Chancellor
Graduate Studies and Research

THE POLYTOPICITY OF IONIC TERNARY COMPOUNDS

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

William Harvey McCulla

June 1981

DEDICATION

The author wishes to dedicate this work to his wife, Bettye, and his children, Allen and Kimberly, whose patience and encouragement during the course of this work was so very much appreciated.

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ABSTRACT

A Raman spectrometer for obtaining spectra of vapors and gases at high temperatures has been constructed. The theories of polytopicity, tautomerism, and fluxional behavior in molecules are described, and a new, more general term, "dynamorphism" (to describe a continuously changing molecular geometry), is suggested as a more general term which includes all the above terms. The Raman spectra of the gaseous tetrahedral molecules CF_4 and OsO_4 have been obtained over the temperature range 300°K to 1361°K. In addition, the Raman spectra of the vapors of Cs_2SO_4 and $MReO_4$ (M = K, Rb, Cs, Tl) have been obtained in the range 1250°K to 1450°K. The ν_1 (908 cm^{-1}), ν_2 (435 cm^{-1}), and ν_4 (631 cm^{-1}) bands of CF_4 were observed, and the effects of temperature up to 983°K on the band shapes and the band intensities were noted. The ν_1 (970 cm^{-1}) and the combined ν_2 and ν_4 (331 cm^{-1}) bands of OsO_4 were observed, and again the effects of temperature up to 1361°K on band shapes and band intensities were noted. The spectra of the perrhenates are all very similar with a sharp band at 970 cm^{-1} and a broad intense band in the 300 to 500 cm^{-1} region.

The structure of the perrhenates in the vapor phase is most likely a tetrahedral anion whose symmetry is unperturbed by the cation, at least within the capabilities of the Raman technique. This conclusion is based upon a comparison of the number and locations of bands observed in the perrhenate spectra with the number of bands expected for the perrhenate ions in C_s, C_{2v}, C_{3v}, and T_d symmetries. The assignment

is reinforced by comparisons with the spectra of the ReO_4^- ion in solution and OsO_4 vapor. Finally, to explain the apparent absence of an effect by the cation on the anion symmetry, it is suggested that the perrhenate molecules in the vapor are polytopic or "dynamorphic" with the M^+ (M = K, Rb, Cs, Tl) residing on a spherical potential energy surface about the anion.

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INTRODUCTION

The chemistry of vapors of simple solid ionic inorganic metal compounds has been of considerable interest for many years. Most of the chemical and structural data for these compounds come from the solid and solution phases but the vapor phase is the only phase in which intramolecular forces are exclusively responsible for the molecular structure of the molecule.[1] Quite often, the structures of the vapor and condensed phases are considerably different owing to the site symmetry effects or the extent of polymerization in the condensed phase.

The importance of vapor phase molecular structure determinations arises from the fact that the structure often refers to free isolated monomeric molecules. The interaction between molecules in the vapor phase is slight and can generally be ignored, as opposed to the condensed phase where packing considerations and nearest neighbor effects must be taken into consideration. These interactions may result in the formation of structures different from the free molecule, particularly where weaker interactions may be perturbed by the intermolecular forces. This may be especially important in ionic compounds in which preferential orientations of the cation-anion groups are perturbed by intermolecular interactions. A specific example typical of ionic compounds is sodium chloride which exhibits a crystalline face-centered cubic structure with each sodium or chloride ion surrounded by an octahedron of six chloride or sodium ions, respectively, alternating throughout the crystal.[2] Each

ion in the bulk crystal is surrounded by a symmetric field whereas in the vapor the linear monomer NaCl or the dimer Na_2Cl_2 exists as discrete units and the molecular symmetry is defined predominantly by intramolecular forces.

Methods employed to study vapor species have included velocity selection, momentum detection, vapor density measurements, mass spectrometry, molecular beam interaction with electrostatic and magnetic fields, electron diffraction, electronic spectroscopy, infrared spectroscopy (vapors and matrix isolated vapors), Raman spectroscopy (vapors and matrix isolated vapors), microwave spectroscopy, and photoelectron spectroscopy.[3] Until fairly recently most of these techniques, particularly the methods capable of yielding geometries, have been limited to the simple gaseous binary compounds, primarily the metal halides. Since the 1960s, serious experimental studies of high temperature vapor species of ternary ionic inorganic compounds consisting of a simple monovalent cation bonded to a complex anion (or vice versa) have been performed.

A. Vaporization of Stable Compounds

Many inorganic compounds are relatively involatile solids at ambient temperatures and may be regarded as bridged polymers or ionic crystals. Thus in order to study the structure of the monomeric species one often has to revert to high temperature techniques.[4] It has been recognized for some time that a variety of ionic ternary compounds can be volatilized without appreciable decomposition.[5]

By ionic ternary compounds it is meant the type $M_mA_aB_b$ where M is a monovalent cation of the alkali metal or alkali type metal (Li^+, Na^+, K^+, Rb^+, Cs^+, Tl^+, Cu^+, Ag^+, Au^+) and A_aB_b is a complex anion (OH^-, CN^-, BO_2^-, NO_3^-, ReO_4^-, BH_4^-, BF_4^-, AlF_4^-, $AlCl_4^-$, $SO_4^=$, $CrO_4^=$, $MoO_4^=$, $CO_3^=$, etc.) where A is a central atom with attached atoms B, the bonding between A and B in the complex anion is predomonantly covalent and the bonding between the cation M^+ and the anion $A_aB_b^{-m}$ is predominantly ionic. Many of the compounds considered have been shown to volatilize while maintaining their molecular integrity, that is to have the composition $(M_mA_aB_b)_n$, where n is only 1 or 2, in the vapor state and to have long term stability as a vapor.

Table I is an extensive list of ionic ternary compounds that have been shown to vaporize without decomposition along with techniques applied for structure determinations. An attempt has been made to cover all the data on ternary gas phase structure determinations through 1980. The abbreviations that are used in the table to indicate the techniques applied are: vapor pressure studies V, mass spectroscopic investigations M, electronic absorption spectra S, infrared vapor studies I_v, infrared matrix isolation studies I_m, Raman spectra R, molecular beam studies Mb, electron diffraction procedures D, microwave absorption spectra Mw, photoelectron spectroscopy P, and theoretical studies T. In a large number of instances fairly high temperatures are required to vaporize the substances and to obtain any appreciable vapor pressure, with compounds having the heavier metal cations tending to be the more volatile. The thallium salts tend to be the most volatile. Also, more specific

TABLE I

IONIC TERNARY COMPOUNDS THAT HAVE BEEN STUDIED IN THE VAPOR PHASE

Compound	Investigational Method and References[a]									
LiOH	V^{6-9}	M^{9-11}	S^{12}	$I_v{}^{12}$	$I_m{}^{13}$	Mb^{13-14}	D^{15}			$T^{11,16-20}$
NaOH	V^{21}	M^{22-23}		$I_v{}^{12,17}$	$I_m{}^{24}$	Mb^{25-27}		Mw^{28}	P^{29}	$T^{18,30}$
KOH	$V^{21,31}$	$M^{22-23,32}$		$I_v{}^{12,17,33-34}$	$I_m{}^{24,35}$	Mb^{25}		$Mw^{33,36}$	P^{29}	$T^{16,34}$
RbOH		$M^{23,37}$		$I_v{}^{12,17}$	$I_m{}^{24}$			Mw^{38}	P^{29}	
CsOH		M^{23}		$I_v{}^{12,17}$	$I_m{}^{39}$	Mb^{27}		$Mw^{36,38,40}$	P^{29}	T^{41}
LiCN		M^{42}			$I_m{}^{43}$					T^{44-47}
NaCN	$V^{48,49}$	M^{50}		$I_v{}^{51}$	$I_m{}^{43}$	Mb^{52-53}			P^{54}	T^{55-56}
KCN	V^{57}	M^{58-59}		$I_v{}^{51}$	$I_m{}^{43}$	Mb^{52-53}			P^{60}	T^{55}
RbCN						Mb^{52}			P^{54}	
CsCN									P^{54}	
$Hg(CN)_2$									P^{61}	
$LiBO_2$	V^{62-64}	M^{65-67}		$I_v{}^{68}$	$I_m{}^{69}$		D^{70-72}			T^{73-76}
$NaBO_2$	$V^{62-63,77-78}$	$M^{65-67,79}$		$I_v{}^{68}$	$I_m{}^{69}$	Mb^{80}	$D^{70,72}$		P^{29}	$T^{73,81}$
KBO_2	$V^{62-63,78}$	$M^{67,79}$			$I_m{}^{69}$	Mb^{80}	D^{72}		P^{29}	T^{82}
$RbBO_2$	V^{83}	$M^{67,79}$			$I_m{}^{69}$		$D^{72,83-84}$		P^{29}	T^{73}
$CsBO_2$		$M^{67,79}$		$I_v{}^{68}$	$I_m{}^{69}$		D^{84}		P^{29}	
$TlBO_2$		M^{85-86}		$I_v{}^{87}$			D^{84}		P^{76}	
$LiCoO_2$		M^{88}								
$LiGaO_2$		M^{88}								
$LiInO_2$		M^{88}								
$LiNiO_2$		M^{88}								
NO_2^-										T^{89-90}
$LiNO_2$		M^{91}								
$NaNO_2$	V^{92}	M^{91}								
KNO_2	V^{92}									
$CsNO_2$				$I_v{}^{89}$						
$RbNH_2$	V^{93}									

TABLE I (CONTINUED)

Compound	Investigational Method and References[a]							
$LiClO_3$				I_m[94]				
$NaClO_3$		M[95]		I_m[94]				
$KClO_3$				I_m[94]				
NO_3^-								T[96,132]
$LiNO_3$	V[92]	M[91]		I_m[97]	D[98]			T[99]
$NaNO_3$	V[92]	M[91]		I_m[97]	D[98]			
KNO_3	V[92]		S[100]	I_m[97,101]		R[97]	P[102]	T[56]
$RbNO_3$	V[92]	M[103]		I_m[97]			P[102]	
$CsNO_3$	V[92]	M[103-104]	I_v[105]				P[102]	T[106]
$TlNO_3$	V[107-108]	M[103,108-109]		I_m[97]	D[110]		P[76]	T[76,111]
$Cu(NO_3)_2$							P[112]	T[112]
$Ti(NO_3)_4$							P[112]	T[112]
$LiPO_3$	V[113-115]	M[116-118]						
$NaPO_3$	V[113-115]	M[117-120]					P[121]	
KPO_3	V[113,115]	M[117-118,122-123]					P[121]	
$RbPO_3$	V[113,115]	M[117-118,124]					P[121]	
$CsPO_3$	V[113,115]	M[117-118]					P[121]	
$TlPO_3$		M[125]						
$AgPO_3$	V[113-115]							
$NaVO_3$	V[126]							
K_2CO_3		M[127-128]						T[132]
Cs_2CO_3		M[127]						T[132]
$LiClO_4$				I_m[129]				T[132]
$NaClO_4$				I_m[129]				T[132]
$KClO_4$				I_m[129]				T[132]
$CsClO_4$	V[130]						P[29]	T[132]
Li_5IO_6	V[131]							
ReO_4^-								T[133-134]
$LiReO_4$		M[135]		I_m[136]				

TABLE I (CONTINUED)

Compound	Investigational Method and References[a]						
$NaReO_4$	$V^{140-141}$	M^{135}	I^{137}	I^{138}		P^{139}	
$KReO_4$		M^{135}	I_v^{137}	I_m^{138}	D^{142}	P^{139}	
$RbReO_4$		M^{135}	I_v^{137}	I_m^{136}		P^{139}	
$CsReO_4$		M^{135}	I_v^{137}	I_m^{136}		P^{139}	
$TlReO_4$		M^{135}		I_m^{136}	D^{143}	P^{76}	T^{106}
$AgReO_4$		M^{135}					
$Ba(ReO_4)_2$		M^{144}					
$Ca(ReO_4)_2$		M^{144}					
$Sr(ReO_4)_2$		M^{144}					
Na_2CrO_4	$V^{145-146}$	M^{147}			D^{148}		
K_2CrO_4	$V^{145-146}$						
Cs_2CrO_4	V^{149}						
Li_2MoO_4		$M^{150-152}$					
Na_2MoO_4		$M^{152-154}$					
K_2MoO_4		M^{154}					
Cs_2MoO_4		M^{153}			D^{155}		
Tl_2MoO_4					D^{156}		
SO_4^-							$T^{132,168}$
Li_2SO_4		$M^{91,157-158}$		$Mb^{91,157}$			
Na_2SO_4	V^{159}	$M^{158,160}$					
K_2SO_4	$V^{161-162}$	$M^{158,163}$		I_m^{164}	D^{165}		
Rb_2SO_4	V^{166}	M^{158}		I_m^{164}			
Cs_2SO_4	$V^{166-167}$	$M^{91,157-158}$		Mb^{27}	D^{169}		
Tl_2SO_4	$V^{170-171}$	M^{171}			D^{172}	P^{76}	T^{76}
Li_2WO_4		M^{173}					
Na_2WO_4		$M^{173-174}$			D^{155}		
Cs_2WO_4							$T^{175-176}$
$LiBH_4$							T^{177}
$NaBH_4$							

TABLE I (CONTINUED)

Compound	Investigational Method and References[a]					
$LiBF_4$						T^{178}
$LiAlF_4$	$V^{179-180}$	$M^{181-183}$	$I_V{}^{184}$	$I_m{}^{185-186}$		T^{187}
Li_2AlF_5	V^{180}	$M^{181,183}$				
$Li_2Al_2F_8$	V^{180}	$M^{181,183}$				
$NaAlF_4$	$V^{188-193}$	$M^{194-195}$	$I_V{}^{184}$	$I_m{}^{185-186}$	D^{196}	P^{29}
$KAlF_4$		M^{197}		$I_m{}^{186}$		P^{29}
K_2AlF_5		M^{197}				
$K_2Al_2F_8$		M^{197}				
$RbAlF_4$				$I_m{}^{186}$		P^{29}
$CsAlF_4$		M^{198}		$I_m{}^{186}$	D^{334}	P^{29}
$Cs_2Al_2F_8$		M^{198}				
$TlAlF_4$		M^{86}				
$LiAlCl_4$	V^{199}					T^{210}
$NaAlCl_4$	$V^{199-201}$					
$KAlCl_4$	V^{202}				D^{203}	
$RbAlCl_4$	V^{199}					
$CsAlCl_4$	$V^{199,204}$				D^{334}	
$CaAlCl_5$		M^{205}				
$CaAl_2Cl_8$		M^{205}				
$CoAlCl_5$		M^{205}				
$CoAl_2Cl_8$		$M^{205-206}$				
$CrAlCl_5$		M^{205}				
$CrAl_2Cl_8$		$M^{205-206}$				
Cu_3AlCl_6		M^{207}				
$CuAlCl_5$					R^{211}	
$Cu_2Al_2Cl_8$		M^{207}			R^{211}	
$MgAlCl_5$		M^{205}				
$MgAl_2Cl_8$		M^{205}				
$MnAlCl_5$		M^{205}				

TABLE I (CONTINUED)

Compound	Investigational Method and References[a]			
$MnAl_2Cl_8$		M^{205}		
NH_4AlCl_4	V^{208}	M^{208}		
$NiAlCl_5$		M^{205}		
$NiAl_2Cl_8$		M^{205}		
$PdAl_2Cl_8$		M^{206}		R^{211}
$SrAlCl_5$		M^{205}		
$SrAl_2Cl_8$		M^{205}		
$FeAlCl_5$		M^{209}		
$FeAl_2Cl_8$		M^{209}		
$InAlCl_4$				R^{212}
$InAlBr_4$				R^{212}
$PdAl_2Br_8$				R^{213}
Other M_mNX_x Ternary Ionic Compounds				
MNX_2				
$NaLiF_2$		$M^{214\text{-}216}$	I^{217}	
$NaLiCl_2$		M^{218}		
$KNaF_2$		M^{216}		
$KNaCl_2$		$M^{218\text{-}219}$		
$RbLiF_2$		M^{216}		
$RbNaCl_2$	V^{220}			
$RbKF_2$		M^{216}		
$RbKCl_2$	V^{221}	$M^{218\text{-}219}$		
$CsRbF_2$		M^{216}		
$CsLiCl_2$		M^{222}		
$CsNaCl_2$		M^{223}		
$CsKCl_2$		M^{223}		
$CsRbCl_2$		$M^{218\text{-}219}$		
$NaAgCl_2$		M^{224}		

TABLE I (CONTINUED)

Compound	Investigational Method and References[a]				
MNX_3					
$LiBeF_3$		M^{226}			
$NaBeF_3$	$V^{230,234-235}$	$M^{228-229,231-233}$			D^{227}
$KBeF_3$	V^{234}				D^{227}
$KMgCl_3$	$V^{236-237}$				
$KCaCl_3$	V^{238}				
$KSrCl_3$	V^{238}				
$KSmCl_3$	V^{238}				
$KYbCl_3$	V^{238}				
$KCrCl_3$		$M^{239-240}$			
$RbCrCl_3$		M^{241}			
$CsCrCl_3$		M^{242}			
$NaFeF_3$		M^{243}			
$LiFeCl_3$	V^{244}	M^{226}			
$KFeCl_3$	V^{244}			$Mb^{245-246}$	
$CsFeCl_3$				Mb^{245}	
$KFeBr_3$				Mb^{246}	
$KCoCl_3$				Mb^{245}	
$CsCoCl_3$			S^{247}		
$KNiCl_3$				Mb^{245}	
$KZnCl_3$		M^{248}			
$NaCdCl_3$	V^{249}				
$KCdCl_3$	V^{249}				
$RbCdCl_3$		M^{250}			
$CsCdCl_3$	V^{251}	M^{250}			
$TlCdCl_3$		M^{252}			
$NaPbCl_3$		$M^{253-255}$			
$KPbCl_3$	V^{249}	$M^{250,253-256}$			
$RbPbCl_3$	V^{257}	$M^{253-256}$			

TABLE I (CONTINUED)

Compound	Investigational Method and References[a]			
$CsPbCl_3$	$M^{251,253-255}$			
$TlPbCl_3$	M^{252}			
Li_2BeF_4	M^{157}			
Na_2BeF_4	M^{228}			
Na_2FeF_4	M^{243}			
MNX_4				
$NaScF_4$	$M^{258-261}$			
$KScF_4$	M^{262}			
$RbCsF_4$	M^{262}			
$NaYCl_4$	M^{263}			
$KYCl_4$	M^{263}			$D^{264-265}$
$RbYCl_4$	M^{263}			
$KLaF_4$	$V^{266-267}$	M^{268}		
$KCeCl_4$	V^{266}	M^{268}		
$KPrCl_4$	V^{266}	M^{268}		
$LiNdCl_4$		M^{269}		
$KNdCl_4$	V^{266}	$M^{268-269}$		
$CsNdCl_4$		$M^{269-270}$		
$NaErCl_4$	V^{271}			
$KErCl_4$	V^{272}	M^{273}		
$CsErCl_4$		M^{270}		
$NaVF_4$		$M^{274-277}$		
KVF_4		M^{278}		
$NaFeF_4$		M^{243}		
$NaFeCl_4$	$V^{200,279-281}$			
$KFeCl_4$	V^{280}			
$AlFeCl_4$		M^{282}		
$LiBF_4$		M^{283}		
$LiGaF_4$		M^{284}		

TABLE I (CONTINUED)

Compound	Investigational Method and References[a]
$TlInCl_4$	V[285]
$PdIn_2Cl_8$	S[286] R[286] D[264]
$NaBiCl_4$	V[287]
Li_2GaF_5	M[284]
MNX_5	
$CuThCl_5$	M[252]
$TlThCl_5$	M[252]
$CuUCl_5$	M[252]
$TlUCl_5$	M[252]
$NaZrF_5$	M[288-290]
$KZrF_5$	M[291]
$CsZrF_5$	M[291]
$KHfF_5$	M[292]
$AlFeCl_5$	M[282]
$AlFeCl_6$	M[282,293]
Cu_2ThCl_6	M[252]
Tl_2ThCl_6	M[252]
Cu_2UCl_6	M[252]
Tl_2UCl_6	M[252]
K_2HfF_6	M[292]
K_2ZrF_6	M[292]
$CsZrF_6$	M[291]
KHf_2F_9	M[292]
KZr_2F_9	M[291]
$CsZr_2F_9$	M[291]

a. The abbreviations that are used in the table to indicate the techniques applied are: vapor pressure studies V, mass spectroscopic investigations M, electronic absorption spectra S, infrared vapor studies I_v, infrared matrix isolation studies I_m, Raman spectra R, molecular beam studies Mb, electron diffraction procedures D, microwave absorption spectra Mw, photoelectron spectroscopy P, and theoretical studies T.

data on a few ternary ionic compounds will be described. These data indicate that many of these compounds have appreciable vapor pressures at high temperatures, exist as the monomer and dimer, and are stable toward decomposition.

All of the alkali metal perrhenates as well as thallium perrhenate can be volatilized without decomposition. The compounds $LiReO_4$, $NaReO_4$, $KReO_4$, $RbReO_4$, $CsReO_4$, and $TlReO_4$ melt at respectively 699°K, 687°K, 828°K, 871°K, 889°K and 800°K.[294-295] Potassium perrhenate has a vapor pressure, determined by the Knudson effusion method, ranging from 0.26×10^{-3} torr at 780°K to 9.6×10^{-3} torr at 853°K.[140] Other vaporization studies indicate that $KReO_4$ begins to sublime below 800°K without decomposition and boils at 1648°K.[141] The other alkali perrhenates resemble the potassium salt in showing appreciable vapor pressures in the range 800°K to 900°K with the $RbReO_4$ and $CsReO_4$ probably the more volatile.[135] The $TlReO_4$ has a volatility similar to those of $RbReO_4$ and $CsReO_4$.

Mass spectrometry has shown the vapor of the alkali perrhenates to consist of monomer and dimer. For $LiReO_4$ the monomer and dimer are in approximately equal amounts at 920°K with only very slight decomposition. The vapor pressures of the decomposition products Re_2O_7 and Li_2O are on the order of 10^3 less than the $LiReO_4$ vapor pressure.[135] Similarly the sodium and potassium perrhenates have shown approximately equal amounts of monomer and dimer at 833°K.[135] The $RbReO_4$ vapor consists of approximately 10% dimer and 90% monomer at 850°K, whereas cesium perrhenate vapor consists of only about 1% dimer and the rest monomer at 840°K.[135] The mass spectrum of $TlReO_4$ shows the vapor to

consist primarily of monomer with only about 3% dimer at 680°K. A small amount of decomposition at this temperature was indicated by the presence of $Re_2O_7^+$ ions.[135]

Other perrhenates such as $Hg_2(ReO_4)_2$, $CuReO_4$, and $AgReO_4$ are known. The mass spectrum of $AgReO_4$ at 900°K indicates principally monomer in the vapor but also contains a large amount of decomposition products.[135] The compounds $Hg_2(ReO_4)_2$ and $CuReO_4$ appear to be even less thermally stable with the $Hg_2(ReO_4)_2$ showing considerable decomposition at 640°K.[135]

The alkali metal cyanides can all probably be volatilized with molecular integrity. The vapors consist of monomer, dimer, and trimer with some smaller amounts of higher polymers but with the dimer predominant. The dimer-monomer ratio probably decreases with increasing atomic weight of the alkali metal and with increasing temperature. Of the other cyanides, Hg apparently does not exist and those of Cu, Ag, and Tl appear to decompose near the melting point.[296-297]

The crystal structure of LiCN indicates that the Li is bound more strongly to the N than the C, indicating that the compound is more properly LiNC or lithium isocyanide. The melting point is also anomalous at 433°K compared to sodium and potassium cyanides which melt at 835°K and 908°K respectively.[48] Ismail, Hauge, and Margrave have shown through mass spectral studies that LiCN vaporizes around 800°K as the monomer, dimer, and trimer.[49] For NaCN the observed mass spectrum of the vapor over the liquid in the temperature range 903-1049°K has shown both monomer and dimer with the dimer predominating.[50] The vapor

pressure of NaCN in this temperature region is in the range of 0.1 torr. Ismail, Hauge, and Margrave have interpreted the IR spectra of matrix-isolated KCN vapors as being composed of monomer, dimer, and higher polymers.[43] Villars reported the vapor pressure of KCN to be in the range 1 to 10 torr at 1143°K.[57] Little data exist on the high temperature behavior of rubidium and cesium cyanides, but it is thought that they resemble the other alkali cyanides.

The melting points of the monovalent cation sulfates are in the order Tl_2SO_4 (905°K),[170] Ag_2SO_4 (929°K),[298] Li_2SO_4 (1132°K),[299] Na_2SO_4 (1157°K),[300] Cs_2SO_4 (1277°K),[300] K_2SO_4 (1342°K),[301] and Rb_2SO_4 (1347°K).[302] The Li, Na, and Ag compounds tend to decompose on melting. The Tl, Rb, Cs, and K compounds tend to vaporize as the monomer and show little tendency to decompose. For K_2SO_4 both Knudson effusion and transpiration measurements indicate that around 1300°K decomposition is not too great.[161] At 1425°K the K_2SO_4 vapor pressure is approximately 0.6 torr whereas the decomposition products' vapor pressure is on the order of 0.05 torr. Above 1500°K the decomposition of K_2SO_4 becomes greater than vaporization. Vaporization of Rb_2SO_4 and Cs_2SO_4 have been studied by Knudson effusion and Langmuir sublimation techniques and shows no appreciable decomposition in the region 1090-1300°K.[166] At 1300°K the vapor pressure of Rb_2SO_4 is about 0.01 torr whereas Cs_2SO_4 shows approximately 0.01 torr at 1220°K. Mass spectral analysis of the vapors of Rb_2SO_4 and Cs_2SO_4 indicate the undecomposed monomer molecule prevalent in the vapor.[158] The Tl_2SO_4 appears to be the most volatile of the sulfates showing appreciable vapor pressure at 1000°K[170] and

little decomposition over the range 973-1233°K.[171] Mass spectral data indicate the principal species present in Tl_2SO_4 vapor is monomer.[171]

The alkali metal and alkali-type metal nitrates melt in the range 479°K for thallium to 687°K for cesium.[303] There is considerable conflicting evidence on their stabilities in the vapor phase but the alkali metal nitrates appear to be stable to 800°K and thallium nitrate to 600°K. Stability of the nitrate vapors appears to be sensitive to impurities, particularly water vapor. Hardy and Field have reported distilling the alkali metal nitrates in the range 723°K to 773°K at 0.005 torr without appreciable decomposition.[92]

Mass spectral data by Büchler and Stauffer,[91] Lauder, Towler and Wieth,[103] Ames,[104] and Cubicciotti[108] indicate that the vapor species of the nitrates are monomer and dimer with about equal concentration for $LiNO_3$ and $NaNO_3$ but primarily monomer for $RbNO_3$, $CsNO_3$, and $TlNO_3$. No mass spectral data were available on KNO_3. Bagarat'yan, Il'in, and Nikitin observed the dimer/monomer ratio for $TlNO_3$ to be about 0.002.[109] Cleaver and Neil have measured the vapor pressure of $TlNO_3$ over $TlNO_{3(l)}$ in the range 523-723°K by both the boiling point and transpiration methods.[107] Cubicciotti made similar measurements on $TlNO_3$ by the effusion method and obtained values approximately 20% lower.[108]

B. Experimental Methods

As outlined in the introduction a large number of methods have been employed to elucidate the structures of vapor species. Many of those methods experience experimental difficulties at high temperature,

and except for simple systems much of the data obtained becomes too complicated to interpret. The most fruitful approaches have turned out to be mass spectrometry, electron diffraction, photoelectron spectroscopy, microwave spectroscopy, molecular interactions with electrostatic fields or electric deflection techniques, and matrix-isolation infrared and Raman spectroscopies. Each of these techniques will be discussed now in more detail and the difficulties with high temperature vapor species structure determination set out.

1. Mass Spectrometry

A first step in the characterization of the vapor phase is the identification of the vapor species. Mass spectrometry appears to be the most versatile method available presently. Once the vapor species have been identified then other techniques can be used to obtain the molecular structures of the gaseous species.[304] A review of Section A will indicate just how extensively mass spectrometry has been used to characterize gaseous species.

The high temperature mass spectrometric technique employs either the Knudson or Langmuir method as a source of the vapor species and uses the mass spectrometer to identify these species. The first reported use of mass spectrometry to determine high temperature vapor species seems to be the work of Ionov who investigated the alkali halides.[305] The work of Chupka and Inghram in 1953 marked the beginning of development of high temperature mass spectrometry and to a large extent the experimental techniques and procedures for data treatment in use today are the results of the work of Inghram.[306]

The process of characterization can be divided into three steps: (a) identification of the ionic species, (b) identification of the vapor species, (c) determination of the amount of each species present. The latter two steps constitute the problem areas of the characterization process. The identification process begins by the association of each ion in the mass spectrum with one or more of the neutral vapor species. This association is often helped by varying the method of ionization and the ionizing potential. But still, a review of the literature on high temperature mass spectrometry shows that species identification can often be very uncertain.[307]

2. Electron Diffraction

Electron diffraction measurements have proved useful in the determination of the interatomic distances in many gaseous species. In a typical experiment a beam of electrons from a hot filament is monochromatized by means of a carefully stabilized accelerating potential. The beam traverses a magnetic focusing system and then passes through a stream of the sample gas. The gas is introduced momentarily into the system through a nozzle and is immediately condensed onto a cold trap on the far side of the electron beam.[308]

Electron diffraction can give accurate values for a limited number of molecular parameters if the symmetry of the molecule is known. However, if the shape of the molecule is unknown, the results are much less certain. In general, the higher the symmetry of the molecule, the fewer the number of internuclear distances to be determined and the more

accurate the deduced molecular parameter. But if the symmetry is uncertain, changes in one parameter can be compensated by changes in others, so that a whole series of slightly different molecular structures may be consistent with the molecular scattering curve.[308]

The interpretation of the electron diffraction patterns of a high temperature vapor also involves a series of complications. From the beginning, electron diffraction by gases has had as its aim the determination of the geometrical configuration of vapor molecules of a definite composition. The association of molecules in the vapor or thermal dissociation of the solid leading to the formation of different compounds stable at high temperatures is not uncommon in high temperature vapors. Thus the vapor phase composition can be in many cases different from the composition in the solid phase. Furthermore, the composition of the vapor coming from the vaporizer may be determined not only by the temperature but also by the conditions of evaporation.[309]

At high temperature considerable difficulty is encountered in the precision determination of internuclear distances by electron diffraction. Here it is necessary to take into account the asymmetry of the potential energy function of the atomic vibrations, and at high temperature the excited rotational and vibrational levels are appreciably populated. The influence of the excited levels on the scattering of electrons is usually neglected in the interpretation of electron diffraction patterns at ordinary temperatures. But at high temperatures it is necessary to develop methods of interpreting electron diffraction patterns which take into account the population of excited molecular energy levels.[309] The

most profound difference between the electron diffraction method and spectroscopic methods for structural determination is in the area of large amplitude vibration. Here electron diffraction observations relate to a thermal average over the populated vibrational states of the molecule.[310]

3. Photoelectron Spectroscopy

In a typical photoelectron spectrometer, a gas or vapor is exposed to a beam of monochromatic radiation, in the VUV or X-ray region of the spectrum, and the photo ejected electrons are analyzed in an electrostatic analyzer. The data obtained are in the form of electron intensity versus electron kinetic energy which is converted to electron intensity versus ionization energy by subtracting the initial photon energy.

To perform photoelectron spectroscopy on high temperature vapors, it is necessary to equip the sample chamber with an oven or similar device to volatilize the sample. This device has been located adjacent to, remote from, and within the sample region with varying success. Techniques for heating have included wire wound resistance heating, laser beam irradiation, and electron bombardment. Some of the special difficulties that arise from the introduction of a high temperature vapor and its means of production within the spectrometer are (a) interference of the magnetic and electric fields by the heating device, (b) deposition of the vapor on cooler surfaces giving rise to uneven charging effects and deterioration of resolution and shifts in peak locations, (c) sample

decomposition and reaction with sample chamber and spectrometer parts, (d) desorption of substances from spectrometer surfaces, (e) non-equilibrium volatilization giving rise to mixtures of species, (f) uneven volatilization resulting in pressure fluctuations producing band intensity and position variations, and (g) vibrational hot-banding of the parent molecule. Many modifications in the instrumentation have been made to help alleviate these problems, but only varying degrees of success have been obtained.

Efforts to ascertain the applicability of PES to the determination of geometries in molecules, particularly the ternary compound vapor monomers, has led to a series of comparisons of empirical results to theoretical calculations. For example, using semi-empirical and ab initio SCF procedures, molecular orbital energy calculations for $CsNO_3$ with C_s, C_{2v}, and C_{3v} symmetry and NO_3^- with D_{3h} symmetry have been performed. As the symmetry is reduced from D_{3h} to C_{3v} to C_{2v} to C_s, splitting of degenerate orbital energies has been seen. This splitting is usually of the order of 0.1 to 0.2 eV. Similar results have been obtained on other compounds. However, in the experimental spectra, band breadths are usually considerably more than 0.2 eV. Thus PES is not presently able to distinguish between the various geometrical possibilities. Also, since it is difficult to tell the difference between band broadening due to pertubation of the symmetry and that produced by the Jahn-Teller effect on ionization, higher resolution PES may still be unable to distinguish between the various symmetry possibilities.[3]

4. Microwave Spectroscopy

Determination of molecular geometry by microwave spectroscopy dates back to Cleeton and Williams' work on NH_3 in 1934.[311] Structural information concerning bond lengths and bond angles in a molecule is obtained from the principal moments of inertia, which are inversely proportional to the rotational constants A, B, C derived from the microwave spectrum. The effective bond length r_0 is obtained from the B_0 or I_0 values for the ground vibrational state and the associated structure is called the r_0 structure. In order to obtain the equilibrium bond length r_e structure, one must extrapolate the r_0 structure to the equilibrium state. To do this the vibration-rotation interaction constant α must be obtained from the microwave spectra of the excited vibrational states. The r_e structure is thus rarely obtained for polyatomic molecules.[312]

To study a high temperature vapor the design of an absorption cell spectrometer must consider several factors which are peculiar to its use at high temperatures. The decrease in conductivity of metals as the temperature is raised, the decrease in resistance of dielectrics and the resultant increase in loss of microwave energy plus the increased chemical activity all must be considered in spectrometer design.[311] Typical spectrometers capable of operating at high temperature appear to have a sensitivity about three orders of magnitude less than the usual room temperature spectrometer.

Since the molecular partition function is large at high temperatures (especially for species with low frequency vibrations such as molecules with heavy atoms), and since the microwave technique typically resolves

rotational levels in the different vibrational states, the individual line intensites will be low.[14] Of course the principal limitation of microwave spectroscopy is that it is useful only for polar molecules. This combined with the fact that in larger molecules the rotational spectrum becomes increasingly complex making reliable assignments almost impossible has limited high temperature microwave spectroscopy to the diatomics.[313]

5. Electrically-Deflected Molecular Beam

The molecular beam electric deflection technique was demonstrated and used by Kallman and Reiche,[314] Stern,[315] Estermann,[316] and others.[317] The ease and reliability of detection of molecular beams by mass spectrometry has been demonstrated by Inghram, Chupka, and their associates in the study of high temperature systems.[306] In high temperature molecular beam experiments there is often uncertainty as to the species present and being examined, and the use of a mass spectrometer as a detector offers considerable advantage. Wharton, Berg, and Klemperer[318] demonstrated the electrical polarity of a molecule by the deflection of a molecular beam by electric quadrupole fields. If a molecule possesses a permanent electric dipole moment, some of the rotational states will show a positive Stark effect, i.e., an increase in energy with increasing electric field. In an inhomogeneous electric field molecules in these states will be deflected against the field gradient toward lower electric field regions. Molecules without a permanent dipole moment will, because of their polarizability, be deflected toward higher field regions. With this arrangement polar molecules may be focused onto the entrance slit

of the mass spectrometer whereas nonpolar molecules will be defocused and show a net drop in intensity.[150] It has been used to study many of the alkali metal oxides and metal halides although this technique is limited to determining whether a molecule possesses a permanent dipole or not. From this the structure is inferred as to whether the molecule has a linear or bent configuration.[14] The technique apparently loses most of its ability to elucidate structure as the molecule becomes more complex.

6. Matrix Isolation Infrared Spectroscopy

An alternative to studying individual molecules as high temperature gases is to isolate them in an inert host matrix at cryogenic temperatures.

Many of the difficulties of attempting high temperature infrared spectroscopy such as reactions with furnace walls, complexity of the spectra due to hot banding and highly excited rotational-vibrational states, and difficulty of achieving a sufficiently high concentration of vapor species for a long period of time, are mitigated or overcome by incorporating a Knudson effusion cell into the matrix isolation spectroscopy technique. The conditions imposed by the matrix eliminate hot bands, excited rotational-vibrational interactions, and rotational fine structure while permitting study of the species without concern for decomposition.[319] This technique is used almost exclusively in the infrared since Raman spectroscopy suffers from the disadvantage of the inherent weakness of the effect.

However, elimination of many of the problems plaguing high temperature spectroscopy by going to matrix isolation leads to uncertainty

as to the true representation of the vapor phase by this technique. One of the major difficulties in matrix isolation is the identification of the species present in the matrix. A further problem, even under ideal conditions, is the guest-host interactions. Little is known about the structure of doped inert gas films. Relatively pure inert gases are likely to deposit as crystalline films in a cubic close packed array. The octahedral and tetrahedral holes in the lattice are too small to accommodate any but the smallest of guest molecules without appreciable interaction. This matrix influence quite often can lead to a lowering of symmetry and the resultant splitting of the degeneracy, and generally manifests itself as line shifts and line broadening in the spectrum. Variations in the matrix environment may simulate the appearance of more than one structure of the trapped species. Impurity concentrations can often be comparable in molar concentrations to the isolated species, particularly from a system where the species is generated at high temperatures. Thus care must be taken in interpreting matrix isolation spectra with regard to vapor phase structure.[4,320]

Most all of the above techniques have been applied to the high-temperature vapors of some ionic ternary compounds, but the elucidation of the structure of the vapor species has been only marginally successful. The use of mass spectrometry to determine the association of the vapor species was outlined in Section A. In the majority of cases involving ionic ternary compounds, the predominant vapor species is a monomer. Electric deflection applied to the monomer vapors of Li_2SO_4 and Cs_2SO_4 has shown them to be nonpolar.[14,27,150] Electron diffraction has been

applied to a large number of complex anion salts and a number of general conclusions can be drawn from the data: (1) features often characteristic of atom pairs involving the cation are missing, even though the cation nuclear charge is of sufficient magnitude, (2) ordinary root mean square amplitudes of the atom pairs of the complex function well to rationalize the experimental data but to fit the cation-anion ligand pair extraordinarily high root mean square vibrational amplitudes are required, 0.20 A versus normal amplitudes of 0.03 to 0.07 A, (3) bond distances between the atom pairs involving the cation can be determined with considerable less reliability than for those atom pairs involving only the complex anion, (4) bond angles in the complex anion are often all equal, within experimental limits, showing no perturbation due to the cation, (5) as the temperature is increased, less usable structural information is obtained, particularly regarding the cation portion, (6) distances from the cation to the nearest anion ligand are larger than corresponding distances in a simple compound of the cation and anion ligand.[73,155-156,227,265] These conclusions have been interpreted to indicate that in high temperature vapors of ionic complex anions, the anion maintains a fairly rigid structure whereas the cation shows considerable freedom of motion.

What infrared studies that have been accomplished on ionic ternary compounds have shown vibrational frequencies of a complex anion almost completely independent of the cation, i.e., all the anion ligands appear equivalent. Also the cation involved vibrational frequencies appear around 100 cm^{-1} or below and are often missing.[12,51,68,137,184] In

matrix isolation IR of vapor species, the lowest frequency modes in the region 120 to 60 cm^{-1} have been assigned to bending modes involving the cation.[24,43,94,97,129,186]

C. Theory: Introduction to Polytopicity

Attempts to characterize high temperature gaseous species have resulted in considerable complications of the experimental data obtained by conventional experimental techniques. A sharp reduction in the amount of useful information obtained, particularly upon increasing the experimental temperature, results in ambiguity in interpreting data in terms of the accepted theories applied to low temperature experiments. Attempts to obviate these difficulties by the combination of different techniques have not led to any significant success. In the simplest case of the alkali metal halides investigation with electron diffraction, electric deflection, matrix isolation IR, and other techniques have not allowed an unambiguous assignment to the structure of these molecules. The principal difficulty appears to be the assumption, in modern structural analysis of molecules, that the concept of a rigid equilibrium geometric configuration (which can adequately describe the space distribution of nuclei in a molecule at low temperatures) can be applied to high temperature systems. But the model has been developed on the basis of low temperature experiments and apparently fails at high temperature.[106]

At high temperatures, particularly if a molecule has some low vibrational frequencies, there may appear in the vapor, structural species whose actual distribution of nuclei may differ in principle from

the equilibrium one. For example, the LiNC molecule which possesses a bending vibration at 119 cm^{-1}, is generally considered linear in its equilibrium low temperature configuration. But since low lying bending vibrations are usually populated first on thermal excitation, at 1500°K the population in the ground vibrational states is approximately 3%, whereas the summary population up to v = 20 is about 70%. The actual distribution density of the lithium nucleus is to a considerable degree spread out in space. Only the ground level possesses a single maximum probability density on the axis through the nitrogen and carbon corresponding to a linear arrangement. But at high vibrational amplitudes the probability density along the equilibrium axis can be quite low. Thus many of the recent theoretical treatments of high temperature vapors attempt to account for the effects of high amplitude vibrations involving the cation.[106]

Both ab initio and semi-empirical theoretical techniques have been applied to the structural determination of the ionic ternary compounds. Ab initio quantum mechanical calculations by Bak, Clementi, and Kortzeborn on lithium cyanide have shown only a marginal energy difference of approximately 0.4 eV between the structural forms LiNC and LiCN with the LiNC being the more stable.[45] Clementi, Kistenmacher, and Popkie have mapped the energy surfaces for a number of geometries of the Li about the CN in nonlinear conformations and have followed the lowest energy path from the LiNC configuration to the LiCN.[46] No energy barrier was found between the LiCN and LiNC linear configuration nor between linear and nonlinear configurations. Thus with thermal excitation of

approximately 0.3 to 0.4 eV, the Li^+ can orbit the CN ion; and no preferred structural configuration in the traditional sense can be assigned. Another way of viewing their conclusion is that Li-N-C bending vibrations have large amplitudes corresponding to high quantum numbers that may bring about an orbiting of the Li^+ about the CN^-. They further predict that this nontypical type bonding of one group orbiting another may be common in high temperature species where excitation energies are sufficient to populate energy levels that permit full orbiting. They introduce the term "polytopic bond," defining it as a bond which essentially has the same energy when it connects atoms in very different positions.[46]

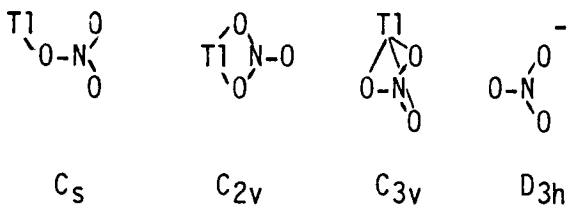
Rambidi, using an electrostatic model, has described the nuclear distribution in complex inorganic molecules in terms of potential energy surfaces. His results on LiCN are very similar to those of Clementi et al. Analyses of $CsNO_3$, $TlReO_4$, and $NaAlF_4$ lead to the conclusion that the metal atom-anion bond could best be described as polytopic in nature. In each case there was a wide range of computational parameters for which the interaction energy varied only slightly for the movement of the cation on an approximately spherical surface circumscribed about the complex anion. Thus only small variations in interaction energy are encountered upon large displacements of the cation relative to the anion along this spherical surface.[106]

Dementjev and Kracht have carried out a quantum mechanical SCF analysis of the $LiBO_2$ monomer. Their results are quite similar to the LiNC calculations with the Li^+ demonstrating large amplitudes of

vibration and a small force constant for this vibration.[75] This molecule may also be described as polytopic.

Rambidi had previously made calculations on the root-mean-square vibrational amplitudes of the MBO_2 (M = Li,Na,Rb) monomers for various temperatures. Comparisons of the values for various atom pairs at 0°K and 1500°K are informative. The root-mean-square amplitude of the Na-O stretching vibration is 0.057 A at 0°K and 0.129 A at 1500°K whereas the comparable B-O stretching vibration is 0.035 A at 0°K and 0.042 A at 1500°K. The ratio of the root-mean-square amplitude at 1500°K to the root-mean-square amplitude at 0°K is 2.26 for Na-O but only 1.20 for the B-O. Similar results have been found for $LiBO_2$ and $RbBO_2$ as well as MCN, MNO_3, $MClO_3$, and M_2SO_4. These results indicate that these compounds constitute a dynamic system in which the alkali metal cation is weakly bonded to a fairly rigid complex anion and exhibits large displacements due to thermal excitations of low frequency vibrations.[73]

In order to assign the peaks in the photoelectron spectra of $TlNO_3$ vapor, and determine whether PES might elucidate the structure, a series of molecular orbital calculations using the ARCANA theoretical program were made by Schweitzer et al.[102] The various configurations for the $TlNO_3$ considered were as follows:



C_s C_{2v} C_{3v} D_{3h}

Distances for the calculations were assigned with the aid of electron diffraction data on the $TlNO_3$ vapor, and the variations in distances and angles have been made in search of minimum energies. The energies and numbers of MOs differed for the different symmetries. The only calculation that fit the experimetal data was the one for the free NO_3^- ion with an independent assignment for the thallium. In all the above cases the molecular structure seems best described by a complex anion whose symmetry is almost totally unperturbed by the cation and a cation-anion association in which the two ions undergo considerable motion with respect to one another.

D. The Fluxional Alternative

An alternative view to polytopic bonding proposed by Clementi et al.[46] to describe nonrigid structures is the more classical approach of fluxional molecules. If we apply the definition of Cotton that if two or more of the possible configurations of a molecule are not chemically equivalent then the process of interconversion is designated isomerization or tautomerization, but if all the configurations are chemically equivalent then the process is described as fluxional, then the latter definition is basically identical to the definition of polytopicity.[32]

The nonrigidity of the molecular structure is the result of vibrational motions, and if these vibrational motions are sufficiently large in magnitude then they may permute the nuclear positions of the molecule. This transition of the system's nuclei from one steric

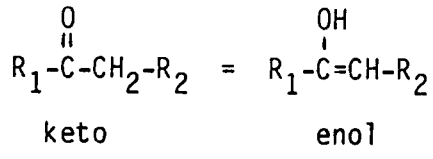
configuration to another constitutes high amplitude motion and the molecules in which such transitions occur are referred to as stereochemically nonrigid or fluxional. In principle, any molecule with identical nuclei can have several steric configurations differing as a result of nuclear transposition provided that these transpositions are not equivalent to a rotation of the molecule. Generally speaking molecules may be characterized by potential functions with two or more minima corresponding to different steric configurations. The depths of the potential functions then govern the ease with which the molecule may move between configurations. If the potential function minima are fairly deep, i.e., provide a high barrier between the minima, then a more definite steric configuration of the nuclei may be assigned which is fairly long lived and may be distinguished experimentally. A transition of the system can occur from one minimum to another by tunnelling through the barrier, but such transitions are not always observed experimentally.

If the thermal energy of the molecule is greater than the height of the potential barrier, then there is an increase in the population of the upper vibrational levels. In order to characterize the geometrical configurations of the molecule when in the high amplitude vibrational state, it is necessary to know values averaged with respect to the vibrations, which usually differ appreciably from the equilibrium values corresponding to the potential minima. The classic example is the ammonia molecule for which there exist two equilibrium configurations arising on reflection of the nitrogen atom through the plane containing the hydrogen

atoms. The vibrational and rotational spectra as well as electron diffraction data can be interpreted in terms of a quasi-rigid pyramidal molecular structure, while tunnelling caused by the inversion induced splitting of the vibrational levels can be observed in the spectra.

If all the potential barriers are very high then one can ignore all the potential minima except one, and the geometric state will be stationary. If the potential barriers are small then the nuclear system does not possess a definite symmetry and cannot be characterized by a stable stationary configuration. As a general rule though, only part of a molecule will experience stereochemical nonrigidity. In most cases the total potential energy function possesses at the same time very high barriers separating the minima from one another plus one or a few low barriers. These low barriers are quite often associated with bending motions in the molecule; and as kT increases, the possibility of crossing the barrier becomes more likely.[322] It is this crossing of the barrier that results in a molecule being described as fluxional.

Tautomerism or fluxional behavior is well established in organic chemistry. The rearrangement of the carbonyl group with an adjacent C-H in what is known as keto-enol tautomerism



is a widely observed mechanism, and sensitivity to temperature of the concentration of the two forms and the rate of conversion between them

has been demonstrated. By careful temperature control the isolations of the pure component of both forms of a number of carbonyl compounds have been accomplished. Additional examples of tautomeric type rearrangements involving organic systems are the ketimine-enamine, ketol-enediol, and lactim-lactam conversions.[323]

Stereochemical nonrigidity is being increasingly recognized in inorganic chemistry, particularly in five, seven, eight, and higher coordinate molecules. The four and six coordinate molecules tend to be far more rigid. However, in considering rigidity the lifetime of a particular structure must be considered. In four and six coordinate molecules the ground state structure generally lies at the bottom of a deep potential well on the potential energy surface. Consequently the energy barrier is very high to rearrangement and the lifetime of the ground state structure is long, e.g., an estimated 10^{15} sec for CH_4. In other molecules with five, seven, eight, etc., coordination, the potential well for the ground state structure is not very deep; and the energy barrier to rearrangement is low. Thus, depending upon the internal energy in the molecule, the lifetimes of a structure (including the ground state structure) may become very short, e.g., ground state lifetimes of 10^{-11} sec for NH_3 and 10^{-5} sec for PF_5 at room temperature. The method of observation and its relative time scale now becomes important. As an example PF_3Cl_2 is consistently in accord with C_{2v} symmetry (with axial Fs) in the infrared and Raman data. But investigation by n.m.r. has detected a large number of low energy intramolecular rearrangements and shows the expected C_{2v} symmetry only below 383°K.[324]

Tautomerism, fluxional behavior, and polytopicity all are special cases of a more general mechanism describing a continually changing molecular geometry. Since the dynamic equilibrium of the molecular structure must be considered, this author proposes the term, dynamorphism, as a general term encompassing the behavior normally depicted by the terms tautomerism, fluxional behavior, and polytopicity. Appropriate prefixes to more fully describe specific behavior in a molecular system with dynamic geometry become possible, i.e., hyperdynamorphism to describe rapidly continually changing molecular structure.

E. Proposed Problem

Although the preceeding sections will attest to the considerable interest in determining the environment and structure of the complex anion in ionic ternary compounds, they also attest to the fact that most of the methods utilized to date have, at best, only alluded to possible configurations and none have been clearly definitive. Of the techniques typically applied to structural determination of gases and vapors, the vibrational spectroscopic techniques seem to have some clear advantages. The effects of symmetry on the observed spectrum has been a fairly successful technique for structure determination and should be applicable to this problem.[325] The interpretation of the spectra, while not trivial particularly at high temperatures, is certainly not as difficult as the problem facing the microwave spectroscopist on similar compounds. Infrared spectroscopy at high temperature, both absorption and emission, can be very difficult, not only in observing the spectrum against a very

high noise background but also in maintaining the cell integrity, in particular that of the windows. Most typical window materials used in the infrared region are not particularly inert, especially at high temperatures. The Raman technique may be able to solve a number of these problems, such as the cell construction where relatively inert high temperature materials (such as fused silica and fused sapphire) can be used. The Raman technique has been applied with considerable success to relatively high temperature vapors.[321] Papatheodorou utilized Raman spectroscopy to study the high temperature vapor complexes of Al(III) and In(III) halides to about 1100°K.[211-213,286] But little has been attempted with the ionic ternary compounds.

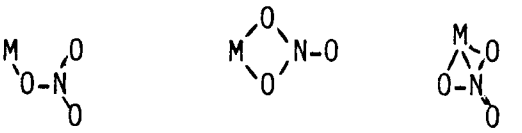
It is proposed that the applicability of Raman spectroscopy to structural determination of vapors in the temperature region where many of the ionic ternary compounds are fairly volatile, namely 1000°K to 1500°K, be ascertained. If this technique is feasible, the high temperature vapor spectra of a number of ionic ternary compounds will be determined and, again, if feasible, structural assignments will be made to the vapor phase molecule. A comparison of the spectra of the ionic ternary compound will be made with high temperature vapor spectra of compounds with known symmetry.

In considering the compounds to be studied, two primary criteria will be evaluated. The first, of course, is whether the compound has an appreciable vapor pressure (10 torr or higher) below 1500°K and is stable in this temperature region. The second is the consideration of the symmetry of the free anion. If the free anion is highly symmetric,

conventional bonding of the cation to the anion should lower the symmetry, break the degeneracy of the vibrational transition, and result in additional bands appearing in the spectrum. It is believed by this author that this appearance of additional bands will be far easier to ascertain than measuring a band shift due to bonding of the cation.

The compounds chosen as meeting the above criteria and listed in the order in which they will be studied are the nitrates, perrhenates, and sulfates of K, Rb, Cs, and Tl. The volatilities and stabilities of these compounds have been well established (see Table I, pages 4-11). The free anions of all are highly symmetric.

The influence of the cation on the anion symmetry can be illustrated by considering the case of MNO_3. The free NO_3^- ion has D_{3h} symmetry; but the metal cation, M, may be assumed to bond in a number of ways to the nitrate anion. Some of these structures and their respective point group symmetry designations are shown below:



C_s C_{2v} C_{3v}

For the trigonal D_{3h} NO_3^- ion, of four possible vibrational bands, three are Raman active. If symmetry is lowered to C_{3v}, and if the metal vibrations are ignored, then there are four possible vibrational bands, all Raman active. With symmetry lowered to C_{2v} or C_s, the degeneracy of the E vibrations (in the C_{3v} structure) are split and six vibrational bands become possible, all Raman active. The T_d point group

symmetry of the free perrhenate and sulfate ions is even more dramatically affected in the number of additional bands that become possible by the lowering of the symmetry. It is hoped that these bands will be prominent enough at high temperatures to allow a symmetry determination and then a decision regarding a possible structure of the vapor molecule. As an additional assist in proving the structure of the vapor molecule, the high temperature spectra will be compared to spectra of a gas or vapor of known structure that is very similar to the anion of interest. For instance, the perrhenate spectra will probably be compared to the high temperature spectrum of OsO_4, a molecule known to be T_d in the vapor and to be very similar structurally to ReO_4^-.

CHAPTER II

EXPERIMENTAL APPARATUS

To obtain the Raman spectra of high temperature vapors, special consideration must be given to the assembly of a Raman spectrometer and sample furnace. The vapor pressures of ionic ternary compounds are still low by normal standards for gas phase Raman spectroscopy at temperatures up to about 1500°K. Thus an excitation radiation intensity as high as possible and a monochromator-detector system with as low noise as possible are required. The materials of construction of the furnace must receive special attention because at 1500°K most materials begin to lose their structural integrity and/or oxidize very rapidly. Operation of the furnace in a vacuum was considered, but fitting such a furnace into the small sample volume available in most spectrometers would have made the design of such a system very difficult.

An arrangement of the Raman system assembled for this study is represented schematically in Figure 1 (p 39) and depicted in Figures 2 and 3 (pp 40-41). The exciting line source is a Control Laser Corporation Model 559A argon ion laser fitted with a Littrow prism wavelength selector and capable of producing 23 watts output multiline and 7 to 10 watts on either the 488.0 nm or 514.5 nm wavelength. The laser is equipped with a servo feedback system to maintain constant output power. The output power level is monitored on a panel mounted meter and the calibration is checked frequently with a Scientech Inc. 36-0001 1 in. surface absorbing disc calorimeter mounted in a 36-0203 isoperibal

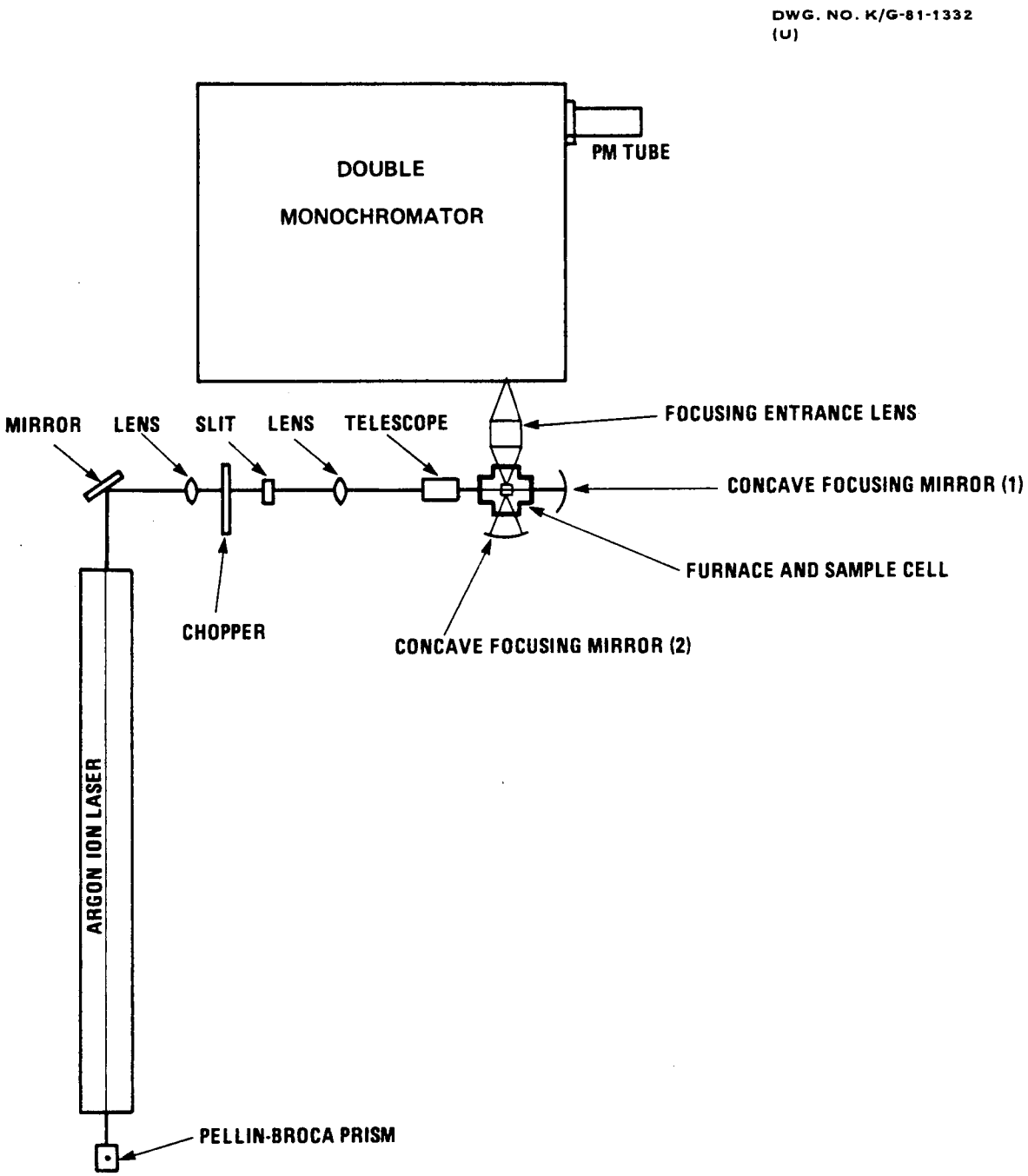


Figure 1. Schematic diagram of the optical system of the Raman spectrometer.

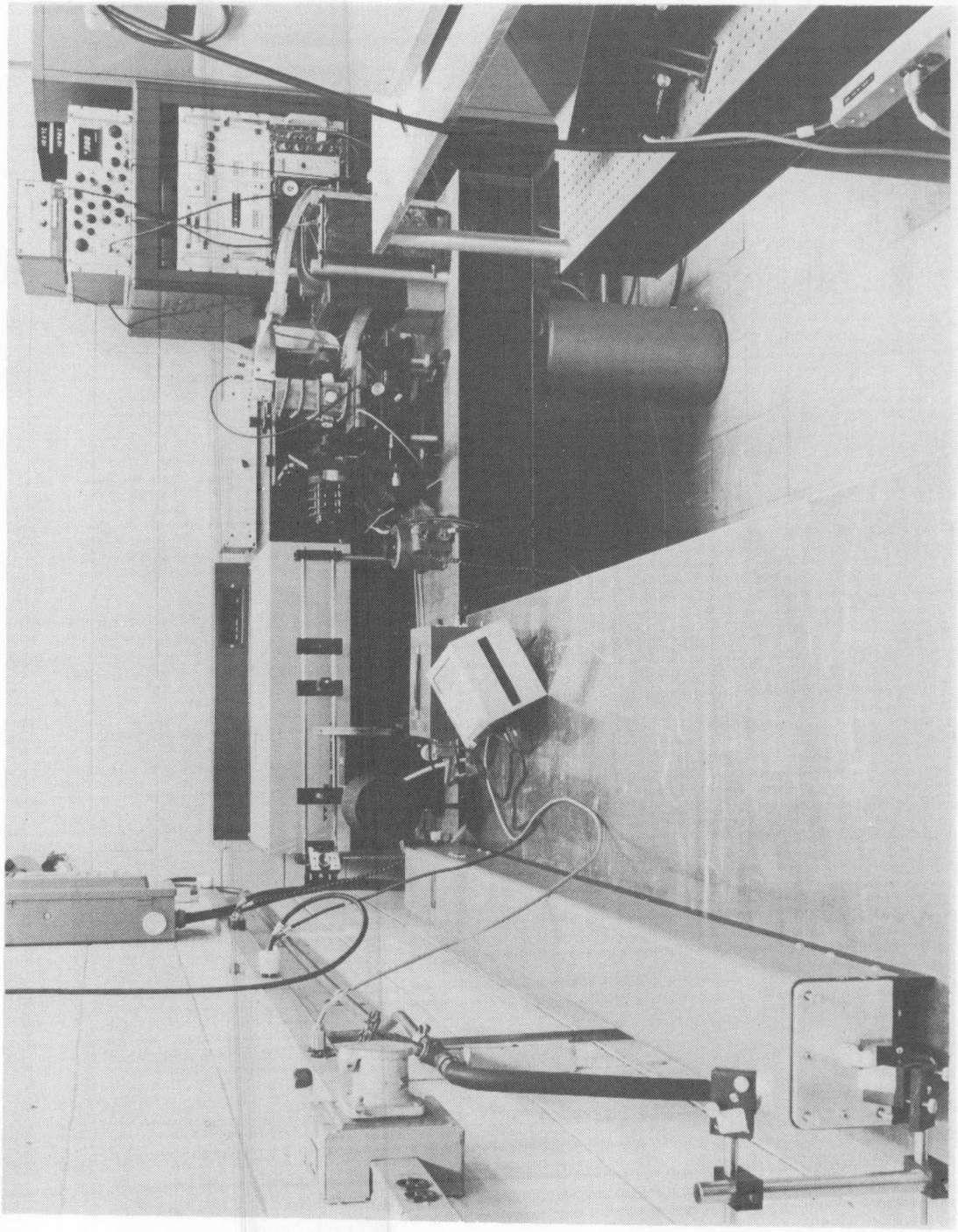


Figure 2. Overall view of laser, optics, and Raman spectrometer.

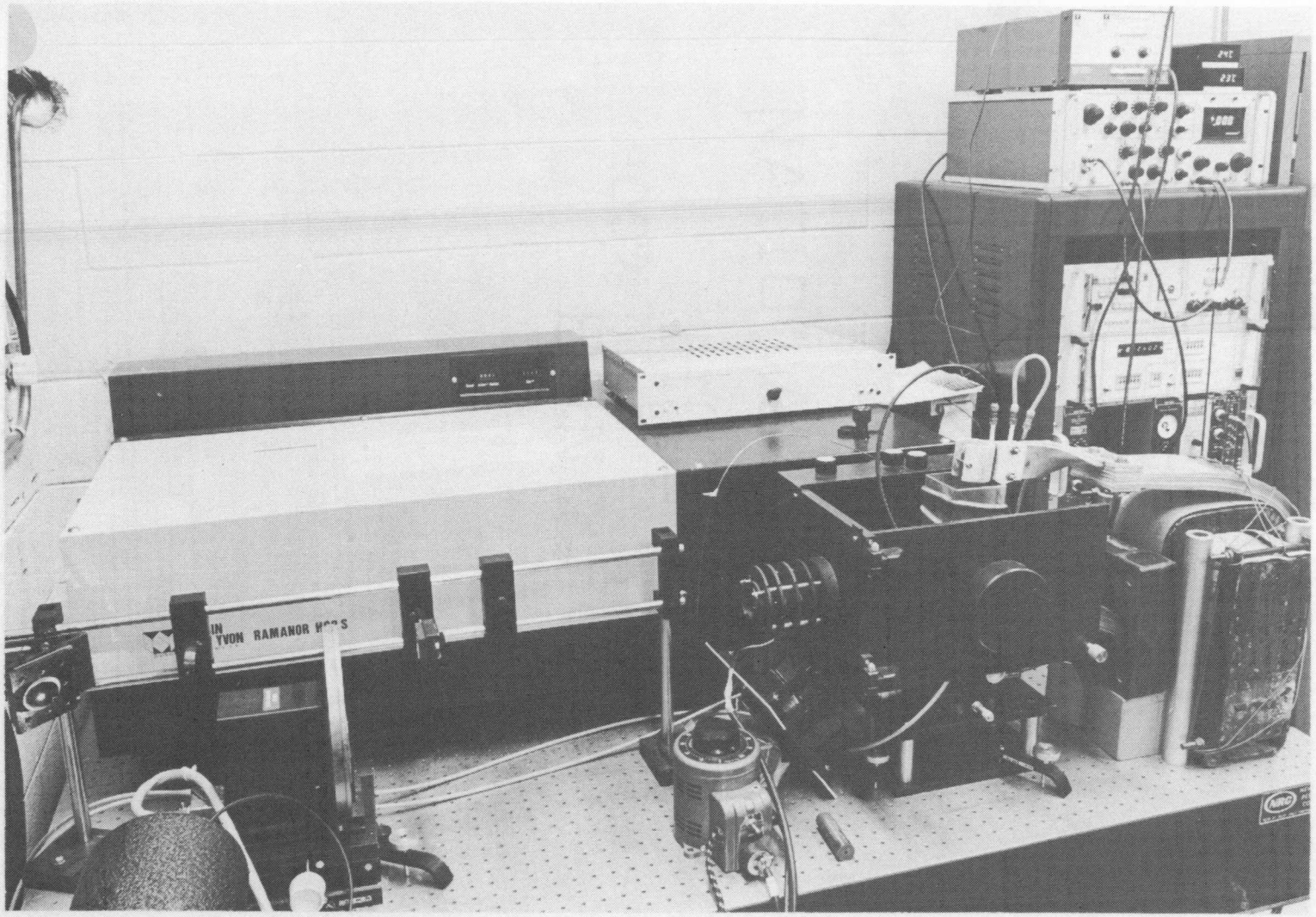


Figure 3. Photograph showing furnace, sample chamber, and Raman spectrometer.

enclosure. The output beam emerges vertically polarized from the laser and is passed through a filter monochromator consisting of two Pellin-Broca prisms mounted one above the other on a Rayleigh mount. This raises the beam to the height of the entrance aperture of the sample chamber, returns the beam 180° from its initial direction exiting the laser, and disperses the light in a vertical plane. Each prism has orthogonal adjustments for movement of the beam in the vertical and horizontal planes. The beam is directed off a dielectric mirror which turns it 90° into the plane of the sample chamber. After 300 cm of travel from the exit port of the laser, the beam enters a 30-cm focal length lens-slit-10-cm focal length lens telescope assembly which removes the dispersed plasma lines, condenses the beam, and transmits the now monochromatic excitation beam. A second telescope assembly located in the sample chamber focuses the beam at the center of the sample cell and the transmitted beam is reflected and refocused to the same spot by the concave focusing mirror (1). Thus the excitation source makes a double pass, with focusing to the same spot on both passes, through the sample region.

The Raman radiation scattered from the region of the excitation beam cross-over point is viewed at 90° and is focused onto the entrance slit of the monochromator by a Berthiat F/1.8, 80-mm focal length compound lens. The sensitivity of the instrument is improved by the reflection and refocusing of the "backscattered" Raman radiation by the concave focusing mirror (2). The double monochromator is a Jobin-Yvon Ramanor HG.2S utilizing 2000 grooves/mm concave holographic gratings.

It is a one meter focal length F/8 aperture instrument with stray light rejection of 10^{-14} or better at 20 cm^{-1} from the Rayleigh line. The monochromator is stepping motor driven in 0.1 cm^{-1} steps and is capable of better than 0.5 cm^{-1} resolution. There are four slits in the instrument, an entrance and exit slit to each monochromator, each controlled separately by a stepping motor. The slits are horizontal, 2 cm long and capable of opening to 2 mm. At 514.5 nm a 100 μm slit opening represents 1.0 cm^{-1} resolution. The exiting Raman radiation from the monochromator is focused onto a Hamamatsu R928 photomultiplier tube mounted in a Pacific Photometric Instrument 3461 thermoelectric cryostat. The photomultiplier is continuously maintained at -30°C and the dark count rate remains typically below 8 counts/sec. An ORTEC 456 High Voltage Power Supply provides 800 volts to the photomultiplier.

A number of furnace designs were considered and several tried.[326-327] The two most severe limiting factors in the design were (1) fitting the furnace within the physical constraints of the volume available without severe modification of the spectrometer entrance optics, and (2) finding a design and materials that would maintain their integrity for extended periods at 1500°K. The final design is represented by Figures 4 and 5 (pp 44-45) and pictured in Figure 6 (p 46). The furnace cell holder [Figure 4 (p 44), and pictured in Figures 7 and 8 (pp 47-48)] is a solid inconel piece machined to take 1-cm quartz fluorimeter cells. It is fitted inside the stainless steel container [Figure 5 (p 45)] with the window ports on the cell holder lining up with holes in the container wall. The region between the cell holder

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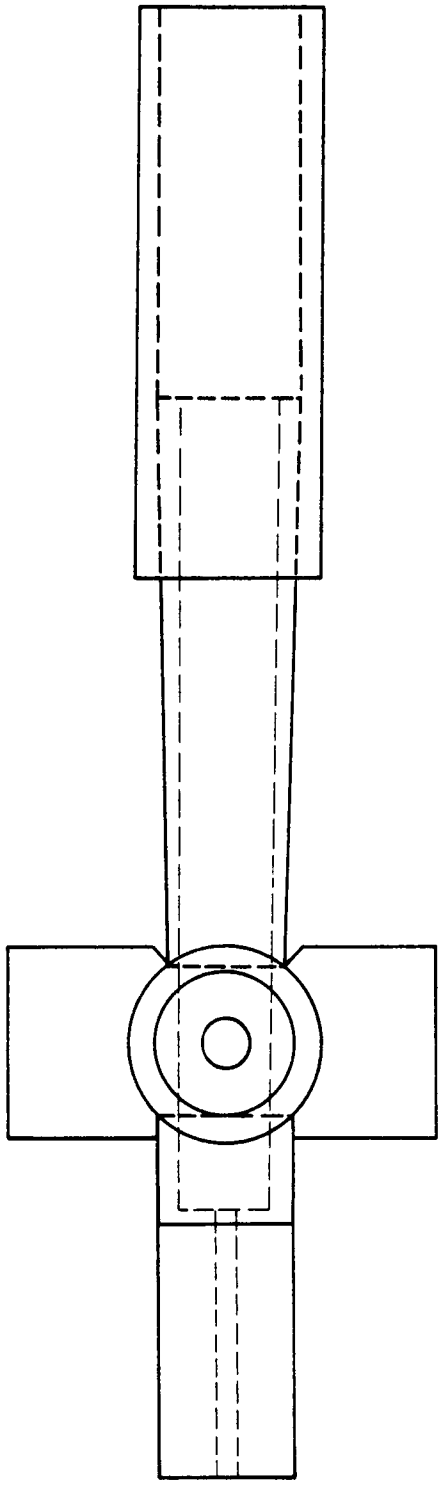

Figure 4. Diagram of furnace cell holder.

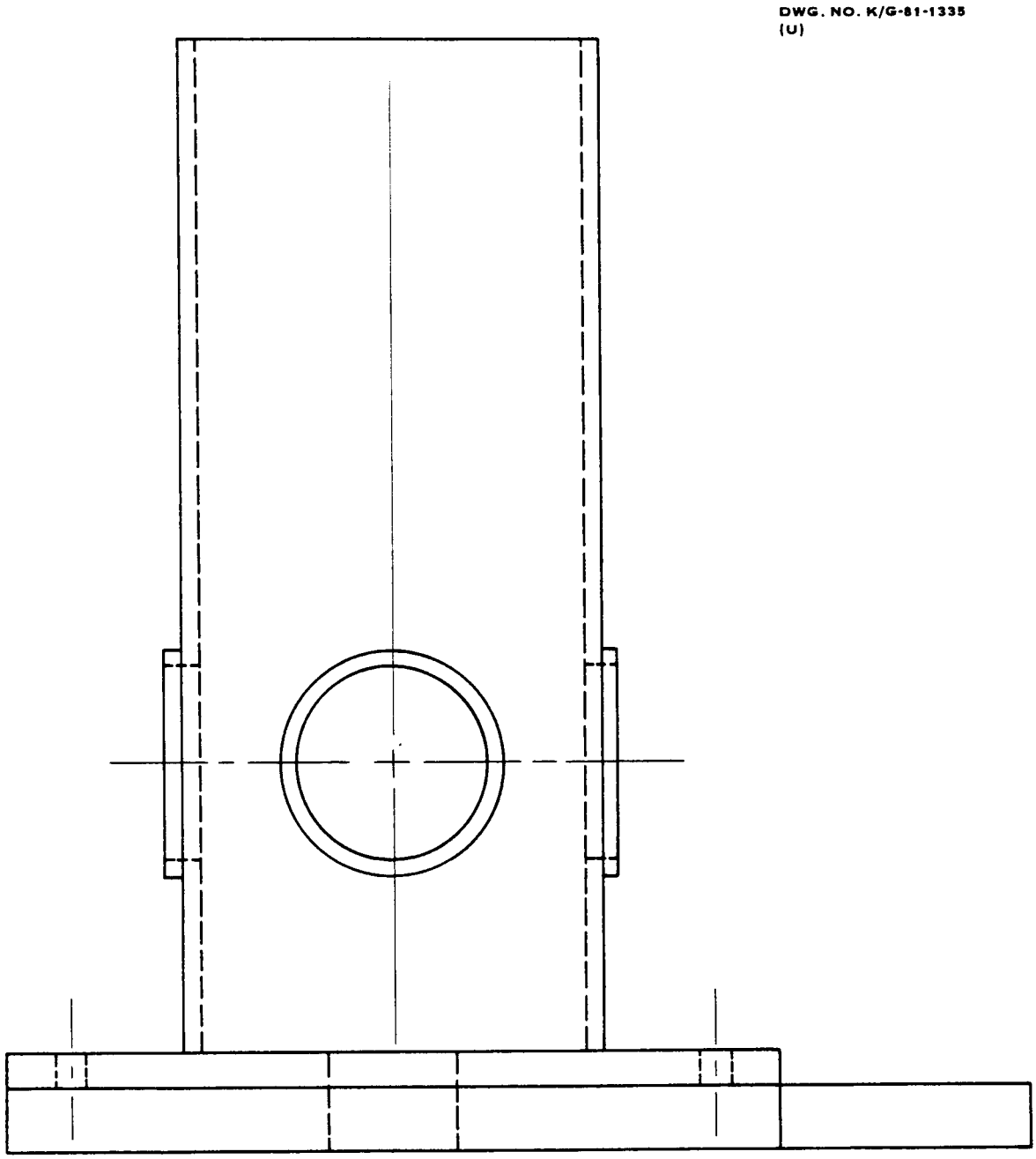

Figure 5. Diagram of furnace container.

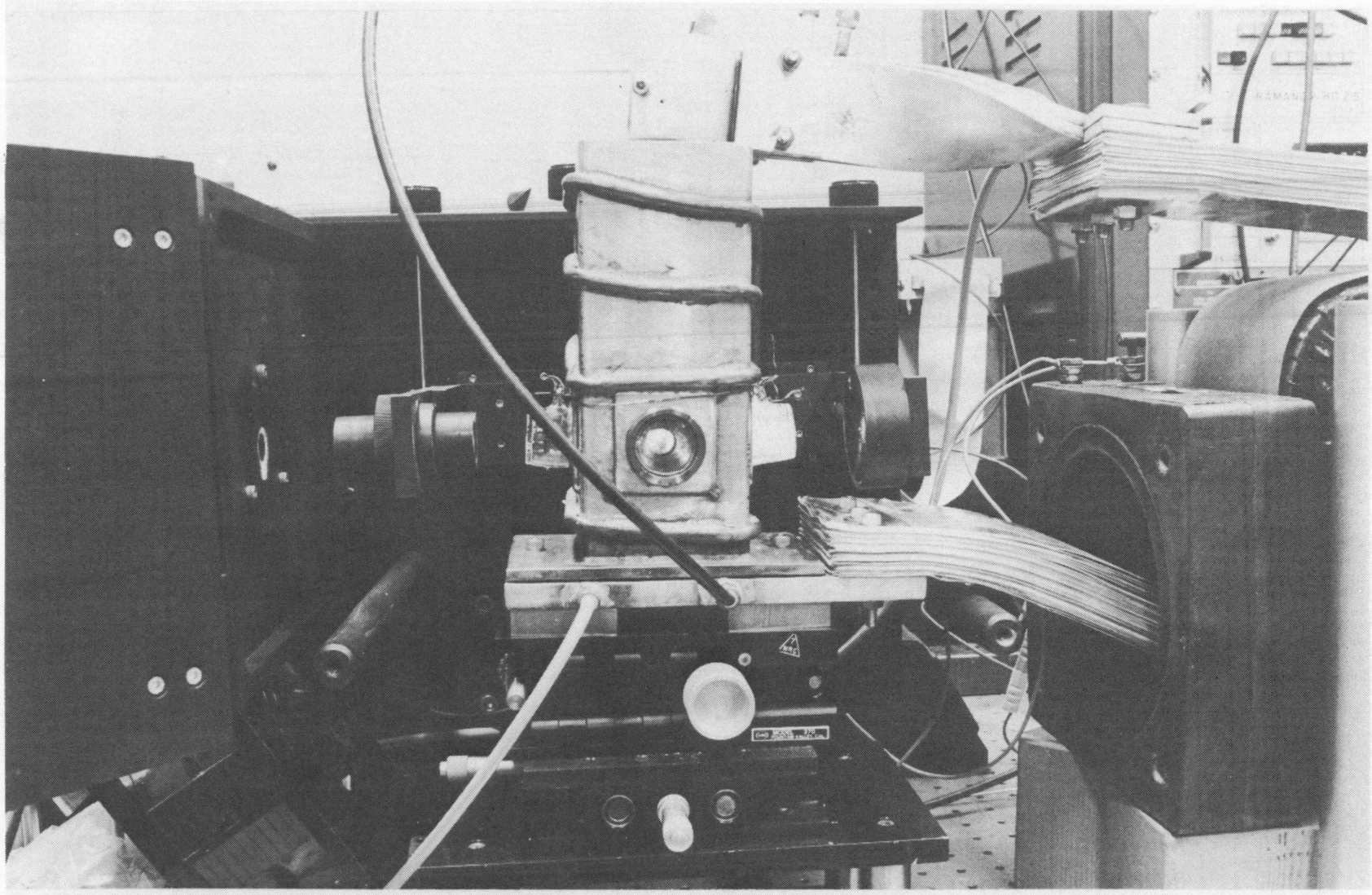

Figure 6. Photograph of assembled furnace in Raman spectrometer sample chamber.

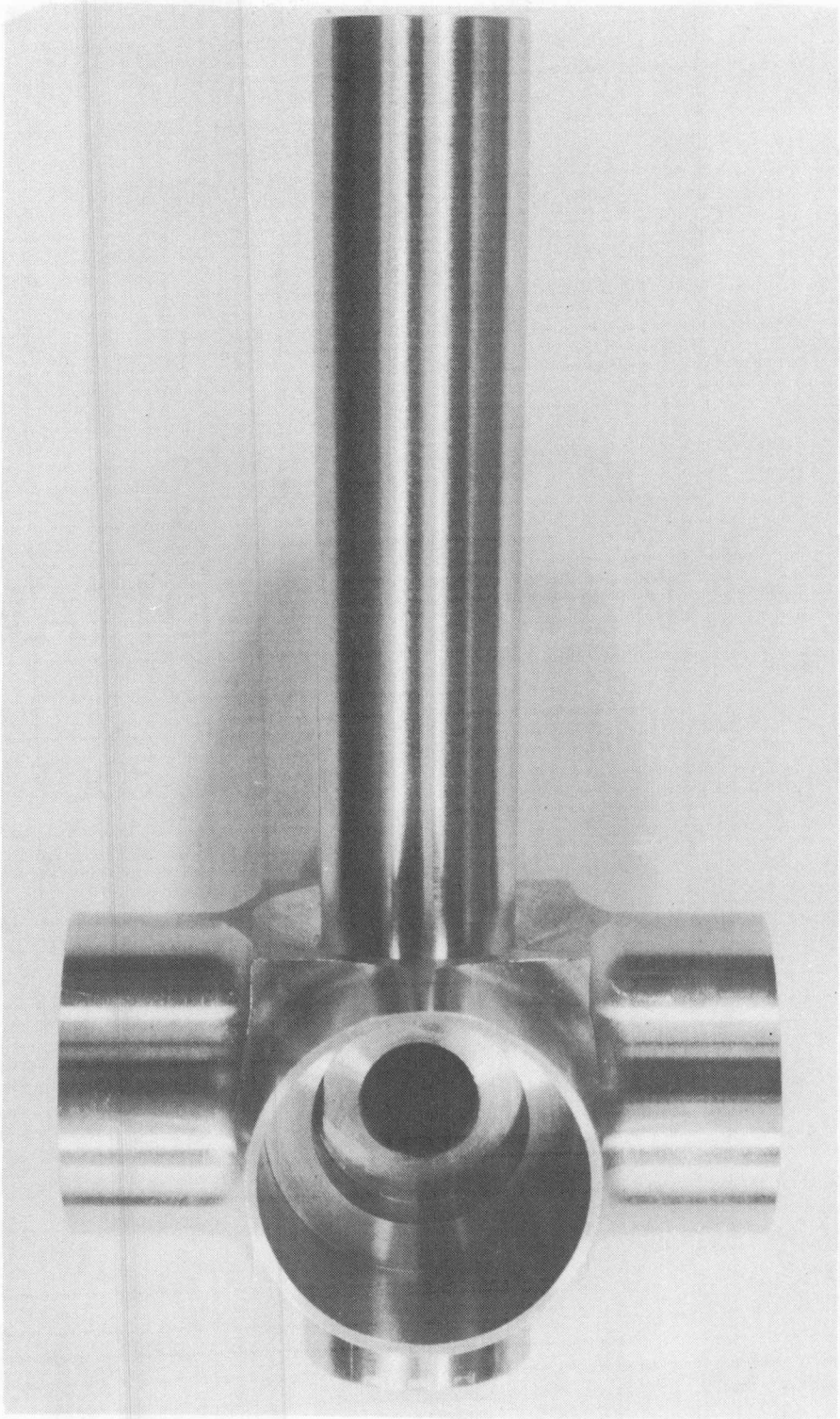

Figure 7. Photograph of inconel furnace cell holder.

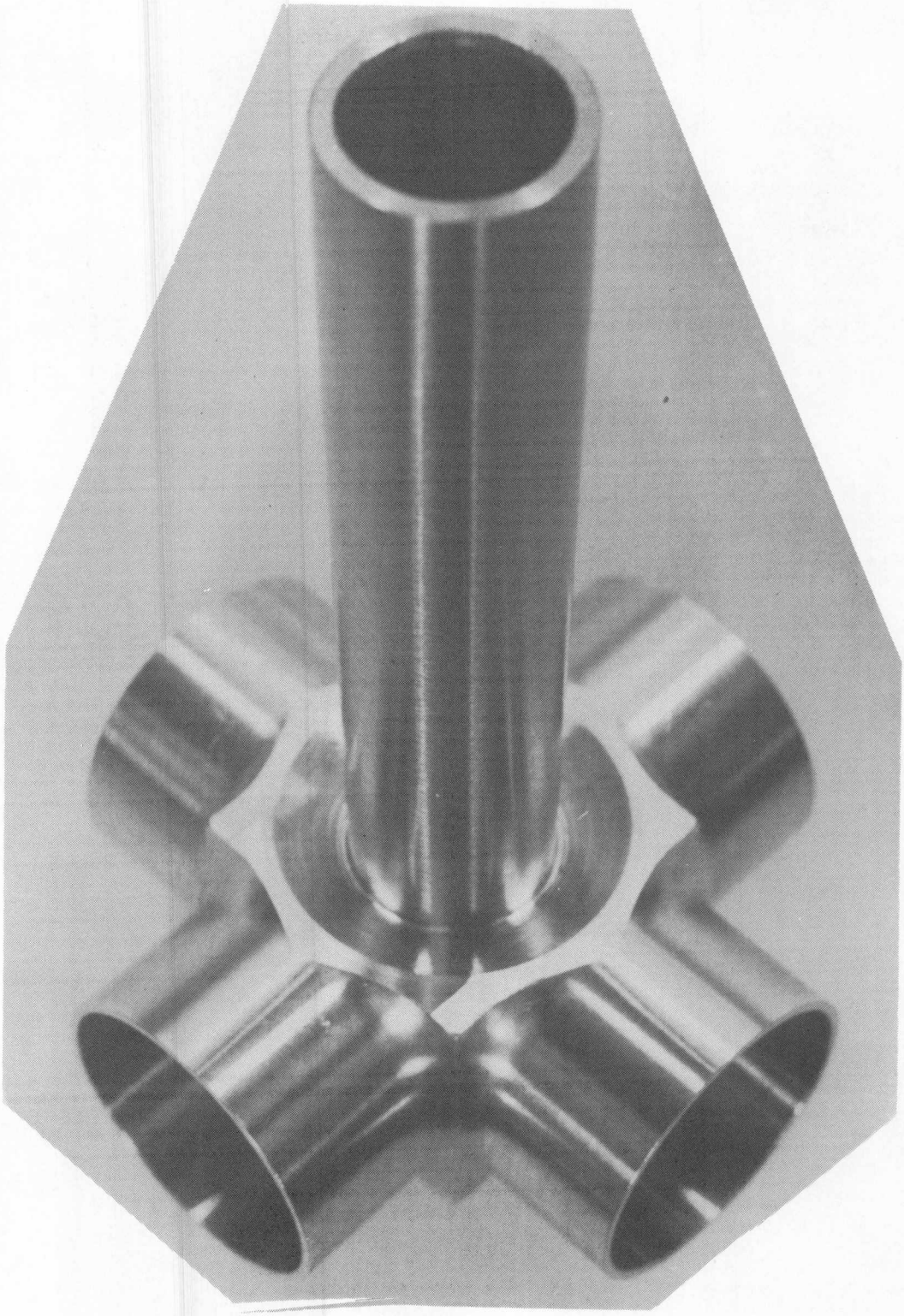

Figure 8. View from above inconel furnace cell holder.

and container is filled with alumina for insulation. Care was taken in the design of the furnace window ports so that the spectrometer would not see any hot wall except that of the central quartz cell. This was done to keep the black body radiation entering the spectrometer to a minimum. Inconel inserts [Figure 9a (p 50)] with quartz windows in each end were initially placed in each window port to act as a thermal barrier, but thermal gradients in the air gap between the windows resulted in a high noise level from flicker of the excitation beam. The all quartz evacuated inserts [Figure 9b (p 50)] replaced the inconel ones and resulted in at least an order of magnitude reduction in the noise level. The furnace is heated resistively by making the inconel cell holder part of an electrical circuit of the secondary of a low voltage power transformer. The transformer is controlled by a Variac in the primary circuit and can provide up to a 1.8 volt drop at 2000 amperes across the inconel cell. The current is monitored by a 2000/5 ratio current transformer in the secondary lead. The lower electrode, container, and upper electrode are water cooled. The assembled furnace, transformers, and busbar connectors are pictured in Figure 10 (p 51). The furnace is mounted on an XYZ translator for positioning. The busbar, connectors, and secondary of the transformer were silver plated to maintain good electrical contact and reduce oxidation. Two stainless steel sheathed chromel-alumel thermocouples were used to monitor the temperature. One was inserted through the hole from the bottom of the cell holder to just beneath the quartz fluorimeter cell [see Figure 4 (p 44)]. The other was inserted from the top beside the quartz cell to

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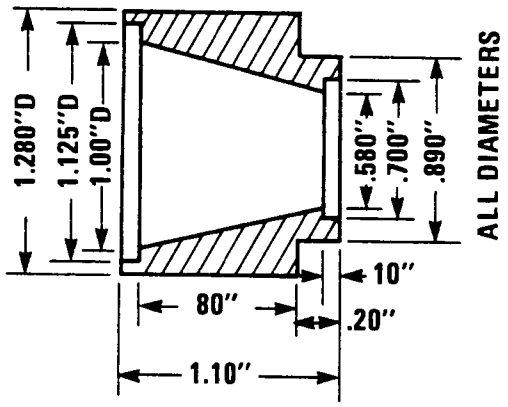
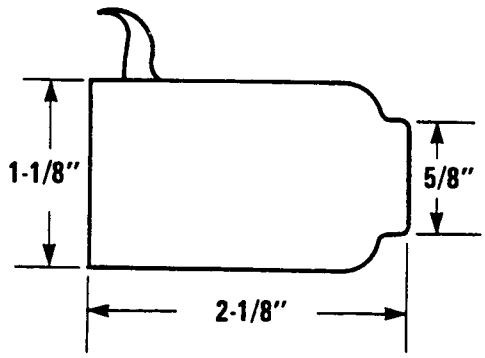


INCONEL WINDOW PORT INSERT
DOUBLE PANE QUARTZ WINDOW
HOLDER

a



DOUBLE PANE QUARTZ
EVACUATED CYLINDER
WINDOW PORT INSERT

b

Figure 9. Diagram of furnace cell window inserts.

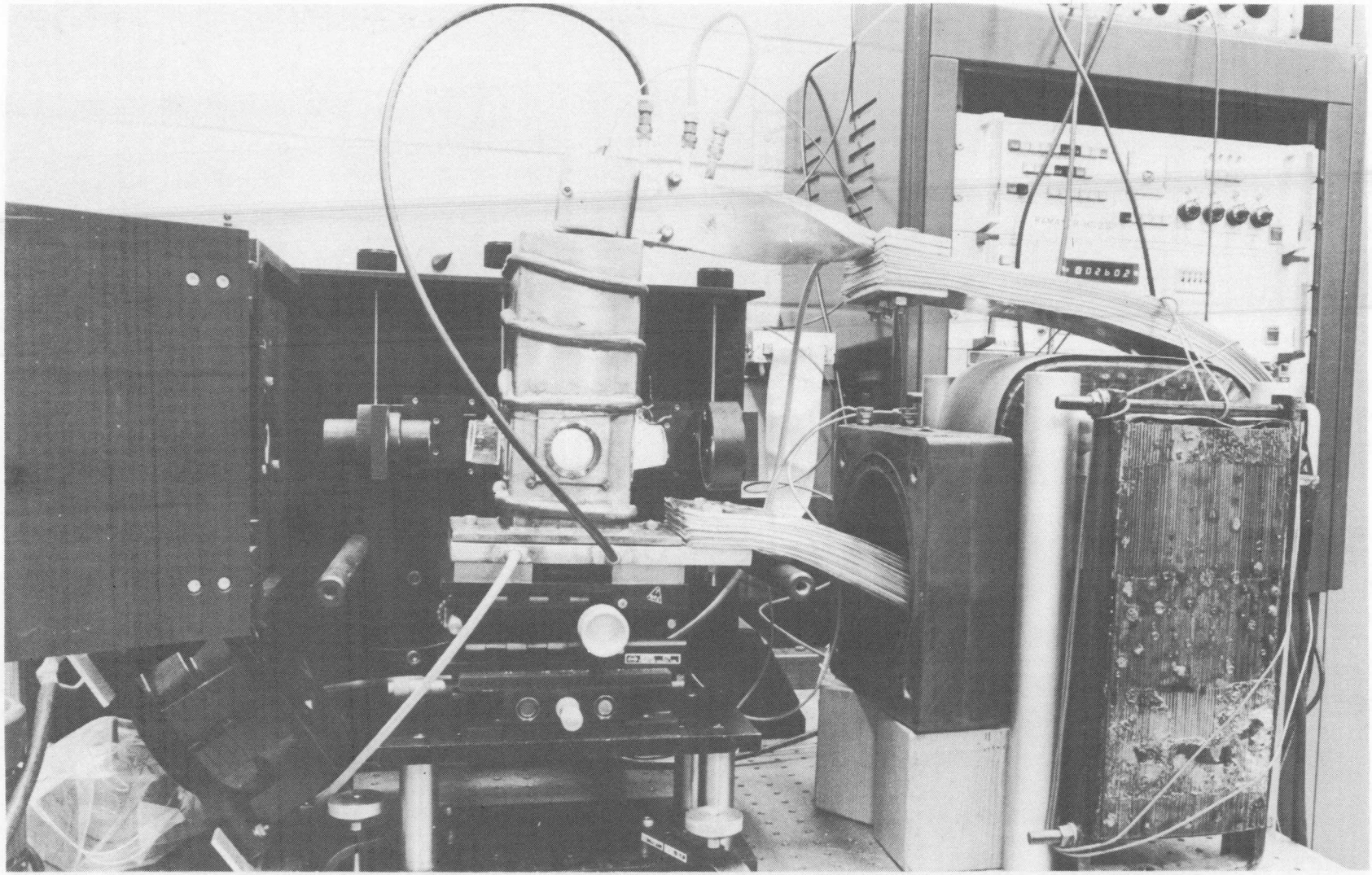


Figure 10. View of furnace and low voltage transformer in the Raman spectrometer sample chamber. The cell is at 1350°K.

just above a window. The temperature was monitored by two Omega 2160A digital thermometers.

Two different electronic arrangements were used for processing the data. The first arrangement is diagrammed in Figure 11 (p 53) and can be employed in data handling up to about 1000°K. The output pulses from the PM tube are amplified and discriminated by a Princeton Applied Research (PAR) 1121 amplifier-discriminator in a single photon counting configuration. The discriminator output is connected to an EGG LG105/N linear gate and stretcher followed by an ORTEC 449 log/lin ratemeter (used primarily during alignment of the Raman signal into the spectrometer), and an ORTEC 550 single channel analyzer. A long lead line to the computer area is followed by a second ORTEC 550 single-channel analyzer to remove line noise and return the pulses to a 5 V level. The data are collected digitally by a Nuclear Data 88-0574 multichannel scaling unit and a Nuclear Data ND-6600 data acquisition and processing system. The Nuclear Data 6600 is equipped with a video display for data presentation and a Pertec hard disk for data storage.

Above about 1000°K the background signal from black body radiation begins to exceed the Raman signal and some means of discriminating and pulling the Raman signal from this background must be found. The technique applied in this study to extend the useful range to 1500°K is diagrammed in Figure 12 (p 54). A PAR 192 variable speed chopper with a two position blade was used to chop the excitation laser beam and provide a reference signal to a PAR 124A lock-in amplifier. The analog output from the PAR 1121 amplifier-discriminator is fed to one side of a

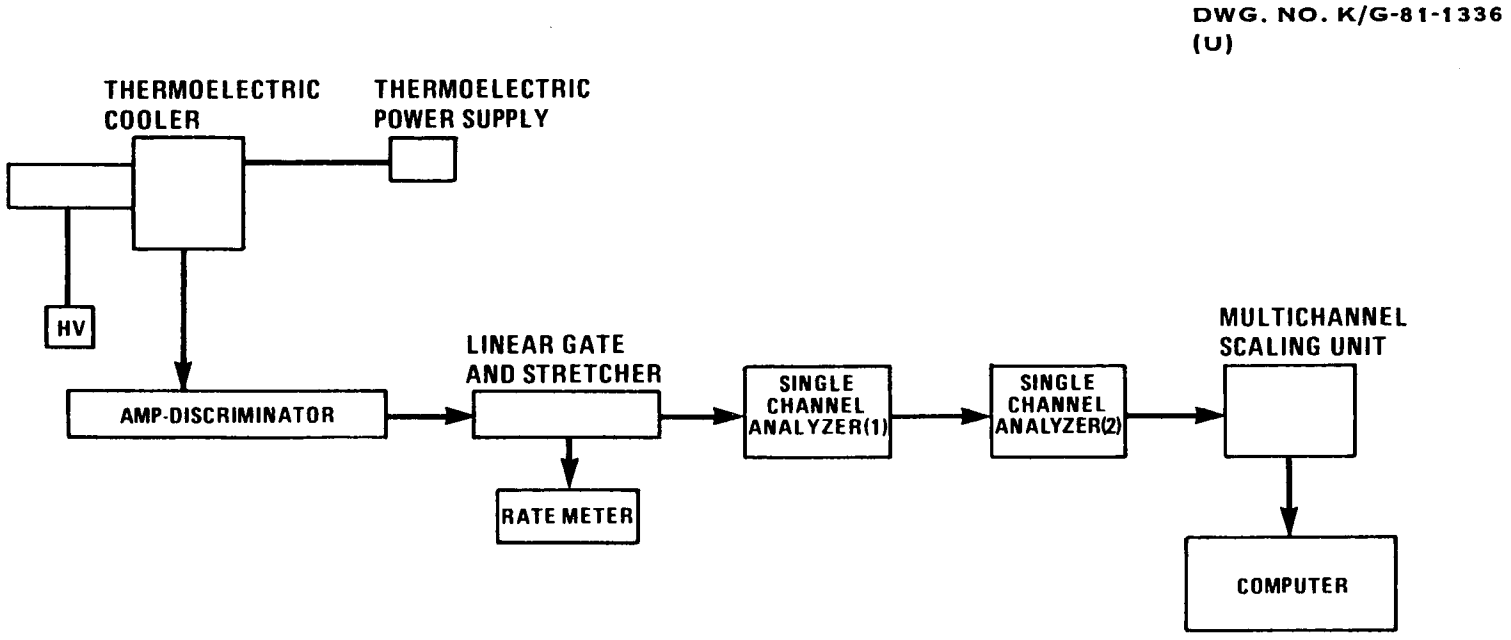


Figure 11. Schematic diagram of electronic configuration for use up to 1000°K.

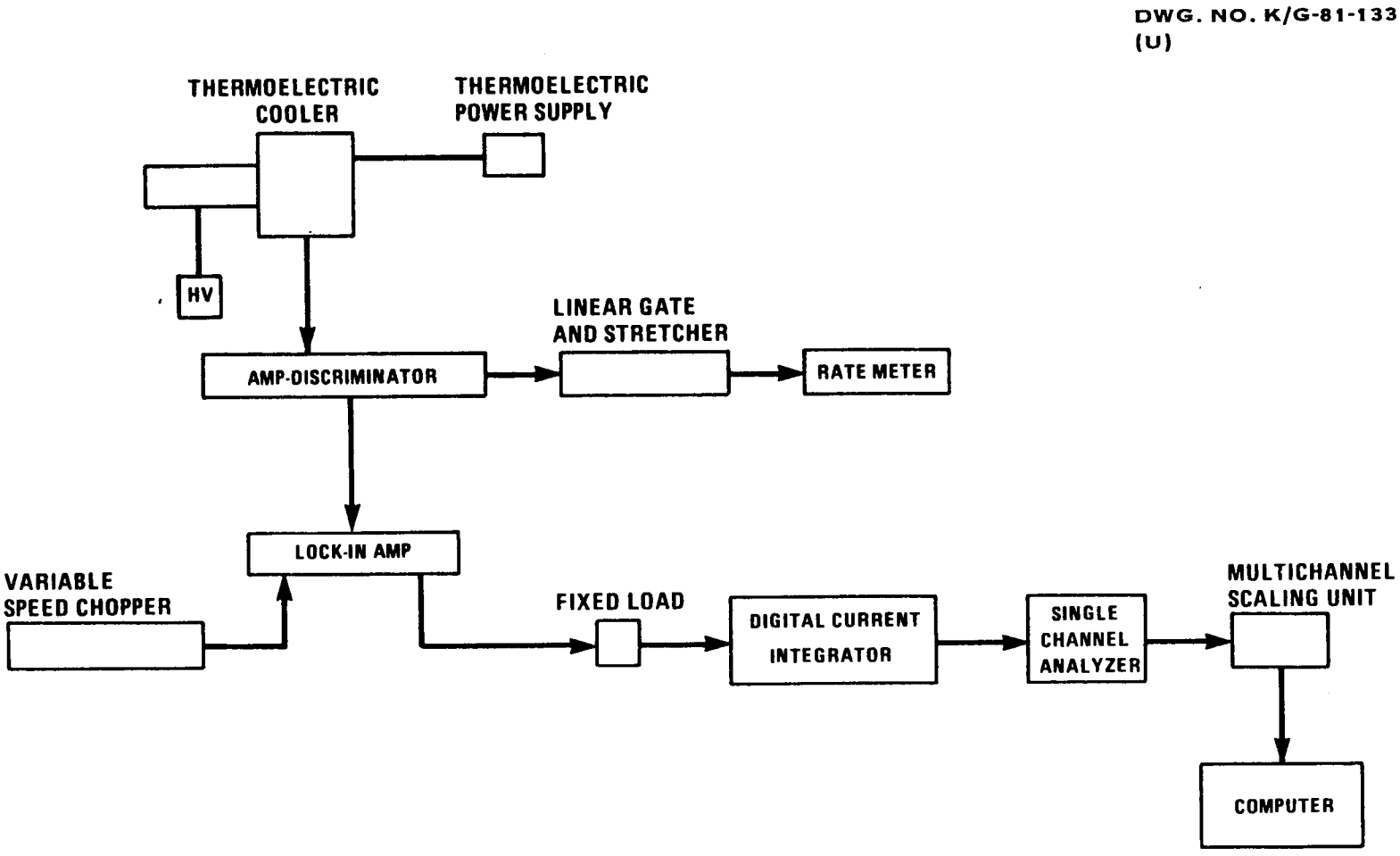


Figure 12. Schematic diagram of electronic configuration for use above 1000°K.

PAR 116 differential preamplifier, operated in the direct mode, and into the PAR 124A lock-in amplifier operated in the bandpass mode with a very high Q. The output of the PAR 1121 is also sent through the EGG LG105/N linear gate and stretcher to the ORTEC 449 log/lin ratemeter. The lock-in amplifier discriminates and amplifies only the signal in phase and frequency with the reference signal from the chopper. Using this technique an approximately 1000-fold signal enhancement could be realized. The analog output from the lock-in amplifier is placed across a 1 megohm fixed load and an ORTEC 439 digital current integrator. This current to frequency conversion provides a digital signal to the ORTEC 550 single channel analyzer, which converts it to a standard 5 V pulse, and is then processed by the Nuclear Data multichannel scaling and data acquisition system. FORTRAN software was obtained along with the appropriate interfaces that allow the computer to control the Jobin-Yvon spectrometer and the multichannel scaling unit.[328] This program provided considerable versatility in the operation of the system through its wide range of scan rates, channel acquisition times, calculation of slit opening for required resolution, and adjustment of slits to the proper setting, plus its data handling and manipulation.

CHAPTER III

EXPERIMENTAL TECHNIQUES

The compounds used in this investigation were obtained from vendors and were used as acquired. The $TlNO_3$ and Tl_2SO_4 were obtained from Pfaltz and Bauer Inc., Flushing, New York, the $CsNO_3$ and Cs_2SO_4 were obtained from Research Organic/Inorganic Chemicals Corporation, Sun Valley, California, the $KReO_4$ from A. D. Mackey, Darien, Connecticut, and the $RbReO_4$, $CsReO_4$, $TlReO_4$, and OsO_4 from the Ventron Corporation, Danvers, Massachusetts. The sample cells were constructed by replacing the graded seals with quartz tubing on type 63 fused silica cells from Precision Cell, Hicksville, New York, and adding a constriction to facilitate sealing the cell.

To prepare a sample for spectroscopy, the empty quartz cell was pumped to approximately 10^{-5} torr and flamed to remove any volatile and reactive materials. On cooling, the cell was backfilled with nitrogen, and about 5 mg of the solid compound to be studied was added. This quantity was ascertained experimentally by determining where condensation on the cell walls ceased at the desired temperature range. The cell was again carefully evacuated to approximately 10^{-5} torr, allowed to pump for several hours, then the cell was carefully flamed all over, except in the region where the compound was located, to be certain it was dry, and finally the region containing the compound was heated until the compound distilled to a cooler section. The cell was then sealed under vacuum at the constriction. Generally a little artistic glass work

was attempted to fabricate a hook during the sealing process. This hook greatly facilitated loading the cell into the furnace. A loaded cell is pictured in Figure 13 (p 58).

Before each spectral run the spectrometer was aligned through the following procedure. The excitation laser source was allowed to warm up for several hours so that its optical cavity would come to equilibrium and diminish output power drift. During this "warm up" period the laser alignment was peaked repeatedly until the laser held a peak power level without further adjustment. This procedure was carried out because the adjustment of the Littrow prism assembly would walk the beam around a large area in the sample region necessitating a spectrometer realignment after each laser adjustment.

Once the laser system had stabilized, centering apertures were placed over the telescope and focusing concave mirror (1) in the sample chamber and the lens-slit-lens filtering assembly removed from the beam path. Then adjustments of the Pellin-Broca prism assembly were made until the beam passed through both apertures, the filtering assembly replaced in the beam and then adjusted until the beam again passed through the apertures. The aperture plates were removed and the focusing concave mirror (1) adjusted until the beam returned upon itself. The position of the furnace was checked to see that the beam passed through the center of the window ports. A needle mounted on an XY translator was placed in the beam near the focus of the entrance lens through a window port, and light was scattered from the tip of the needle. This scattered radiation was imaged on the center of the entrance slit of the

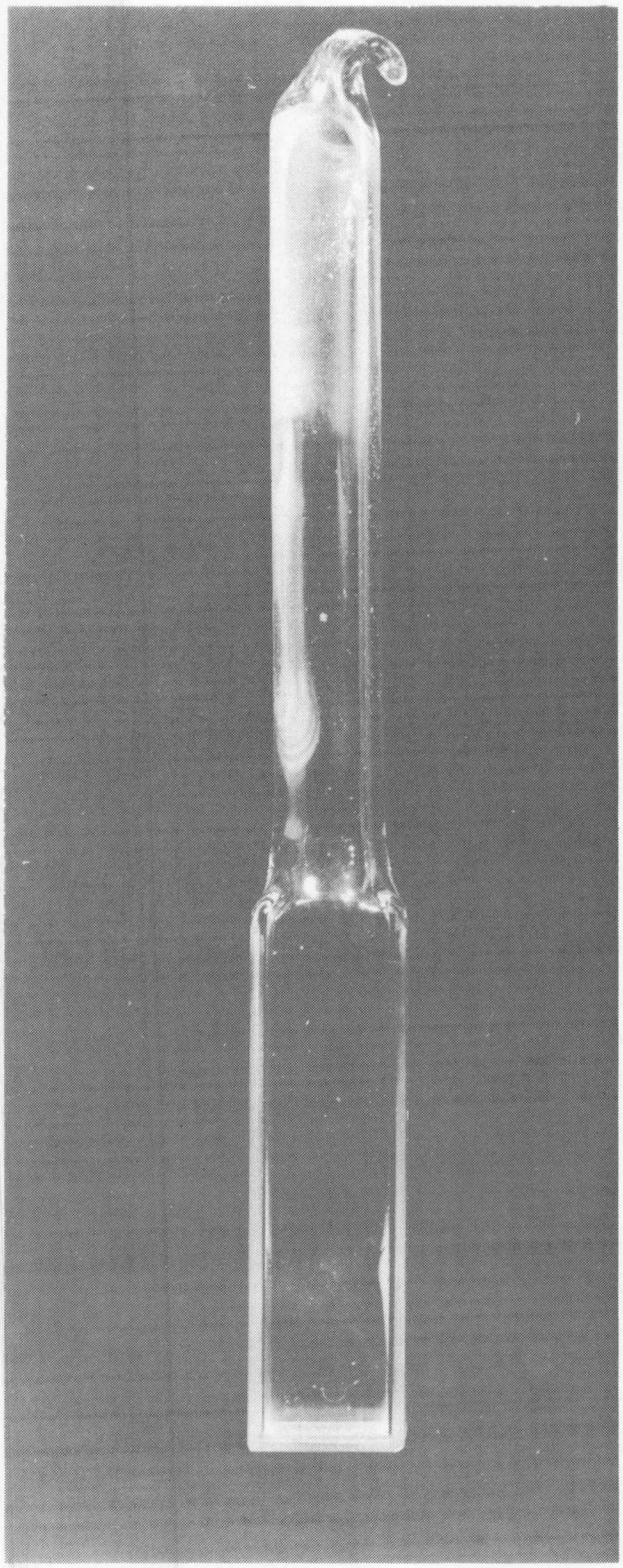


Figure 13. Photograph of typical sample cell.

first monochromator by adjusting the position and focus of the entrance lens while observing through a periscope assembly on top of the monochromator. This provided a rough alignment of the monochromator. The fine adjustment was performed by setting up on the Q branch of nitrogen at 2331 cm^{-1} and peaking the response as indicated on the ratemeter. This would complete the alignment if the electronics configuration in Figure 11 (p 53) was used. If the configuration in Figure 12 (p 54) was used, the lock-in amplifier also had to be aligned. This alignment just adds the following steps to the procedure outlined above. After the fine alignment of the spectrometer on the nitrogen Q branch, the chopper was turned on and allowed to stabilize. The center frequency for the bandpass on the lock-in amplifier was then adjusted until maximum response for the nitrogen Q branch was observed at the lock-in amplifier output. The sample cell was lowered into the cell holder, and current applied to the cell holder incrementally until the desired temperature was reached. Fine adjustments were then made to the current level until the temperature stabilized in the desired temperature region.

The time constant chosen for the lock-in amplifier was 30 sec based on experimental results on noise reduction at high temperature while scanning the 2331 cm^{-1} nitrogen Q branch. This long time constant necessitated fairly slow scan rates, typically around 3 cm^{-1}/min, which were determined both by scanning the nitrogen Q branch at room temperature and comparing the band shape to the known band shape and by calculating the rate from data provided in the lock-in amplifier manual.[329]

The excitation line choice was arrived upon by similar techniques. In Figure 14 (p 61) the black body radiation curve at a temperature of 1225°K from 17036 cm^{-1} to 20108 cm^{-1} is presented with a marker at the 19432 cm^{-1} (514.5 nm) position of a strong argon ion laser line. In Figure 15 (p 62) the continuation of the curve from 20108 cm^{-1} to 23180 cm^{-1} with a marker at 20492 (488.0 nm) is presented. A comparison of the relative heights of the line indicates an approximately 2/1 improvement in signal to noise at the 488.0 nm position. Since, with the argon ion laser available for this study, the power available from the 488.0 nm line was generally greater than 3/4 that of the 514.5 nm line, and with the $1/\lambda^4$ factor in the scattering intensity favoring the 488.0 nm radiation, the 488.0 nm line was chosen. This choice was proven correct by comparison of results for the two lines on the nitrogen Q branch.

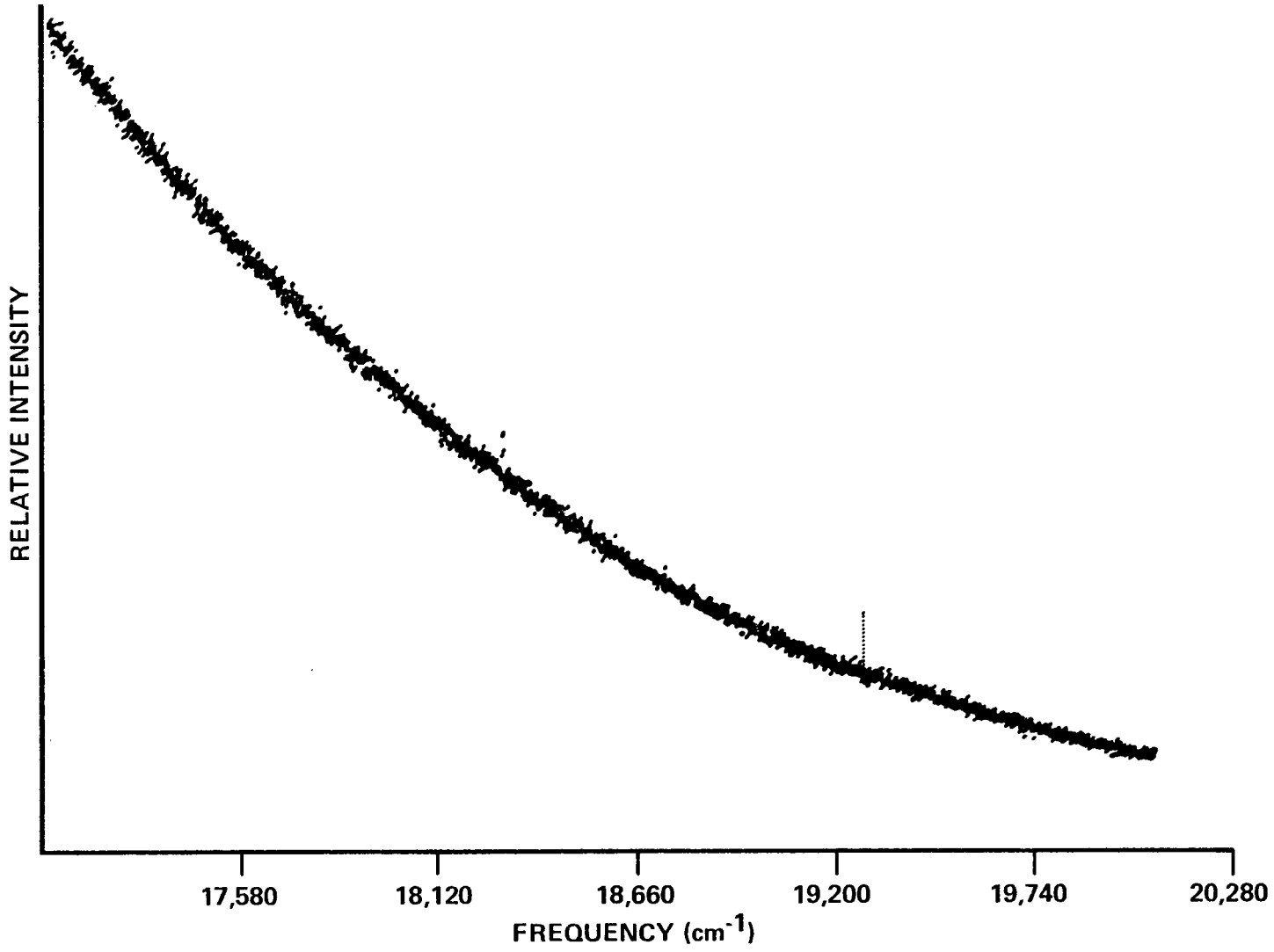


Figure 14. Background black body radiation from sample cell at 1225°K.

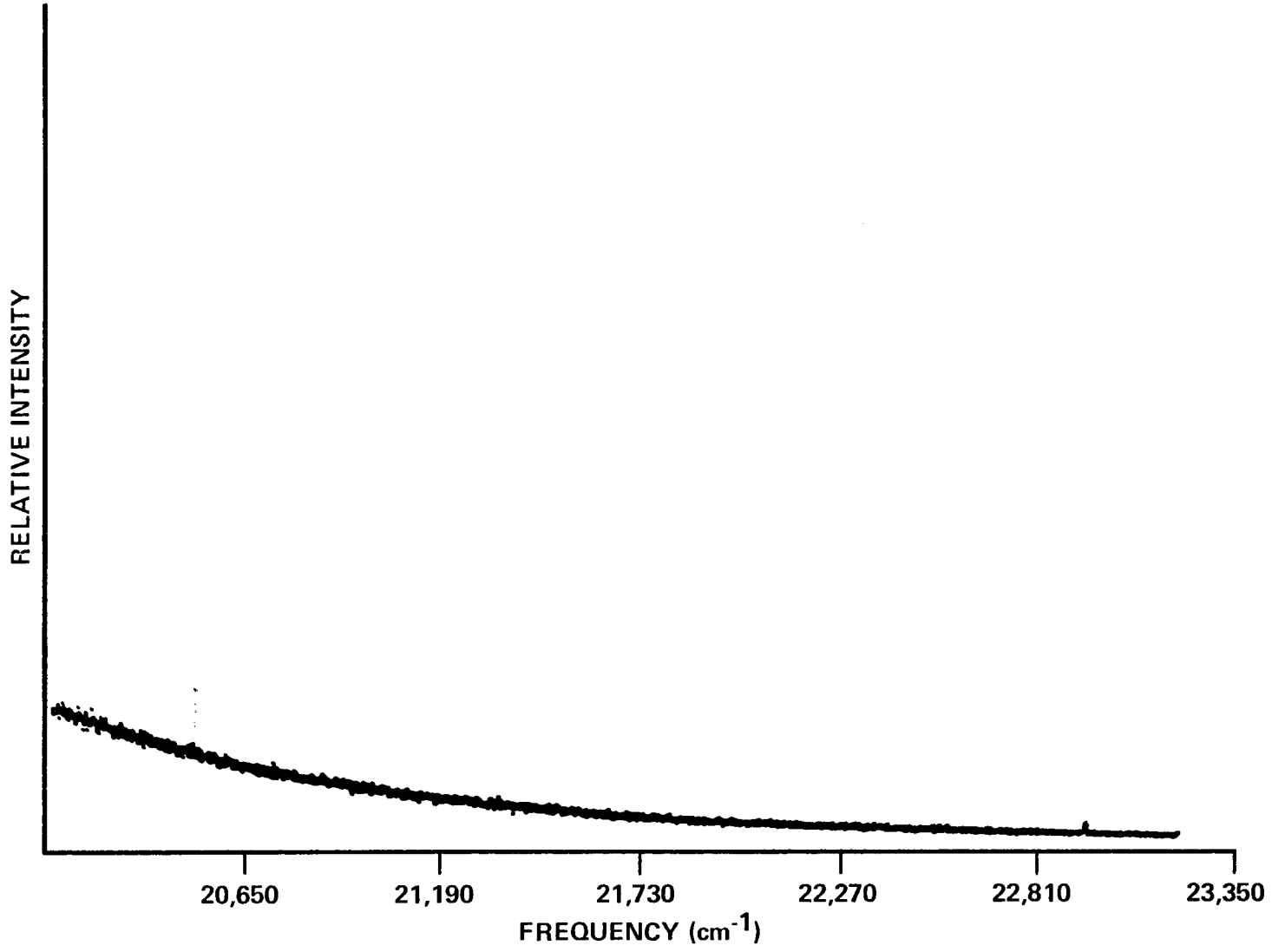


Figure 15. Continuation of background black body radiation from sample cell at 1225°K.

CHAPTER IV

EXPERIMENTAL RESULTS

Figures 16 through 37 (pp 64-85) present representative Raman spectra taken during this study. Tables II, III, and IV (pp 86-88) list the spectrometer parameters for the spectra of the figures listed. Spectra of CF_4 were run to determine the effects of temperature on broadening and band shape, particularly with respect to the bending modes, on the appearance of hot bands, and to serve as a test of the technique. Attempts were made above 1100°K but CF_4 apparently begins to react with the quartz cell around this temperature. As outlined in the proposed problem, the spectra of the alkali metal and thallium nitrates were attempted first because of their much greater volatility than the perrhenates or sulfates. Both thallium and cesium nitrates were tried in the temperature range 925 to 1050°K, but in both cases the long term stability of the nitrates to decomposition was not sufficient to obtain spectra. The concentration of one of the decomposition products, NO_2, was measured by UV-Vis absorption techniques in the sealed sample cell, and the measurements indicated almost complete decomposition.

The spectra of the perrhenates of K, Rb, Cs, Tl were determined in the temperature range 1225°K to 1450°K. All, with the exception of $KReO_4$, were stable to decomposition. The $KReO_4$ decomposed very slowly as evidenced by the anti-Stokes spectrum [Figure 28 (p 76)] which resembles all the other perrhenate spectra but the appearance of

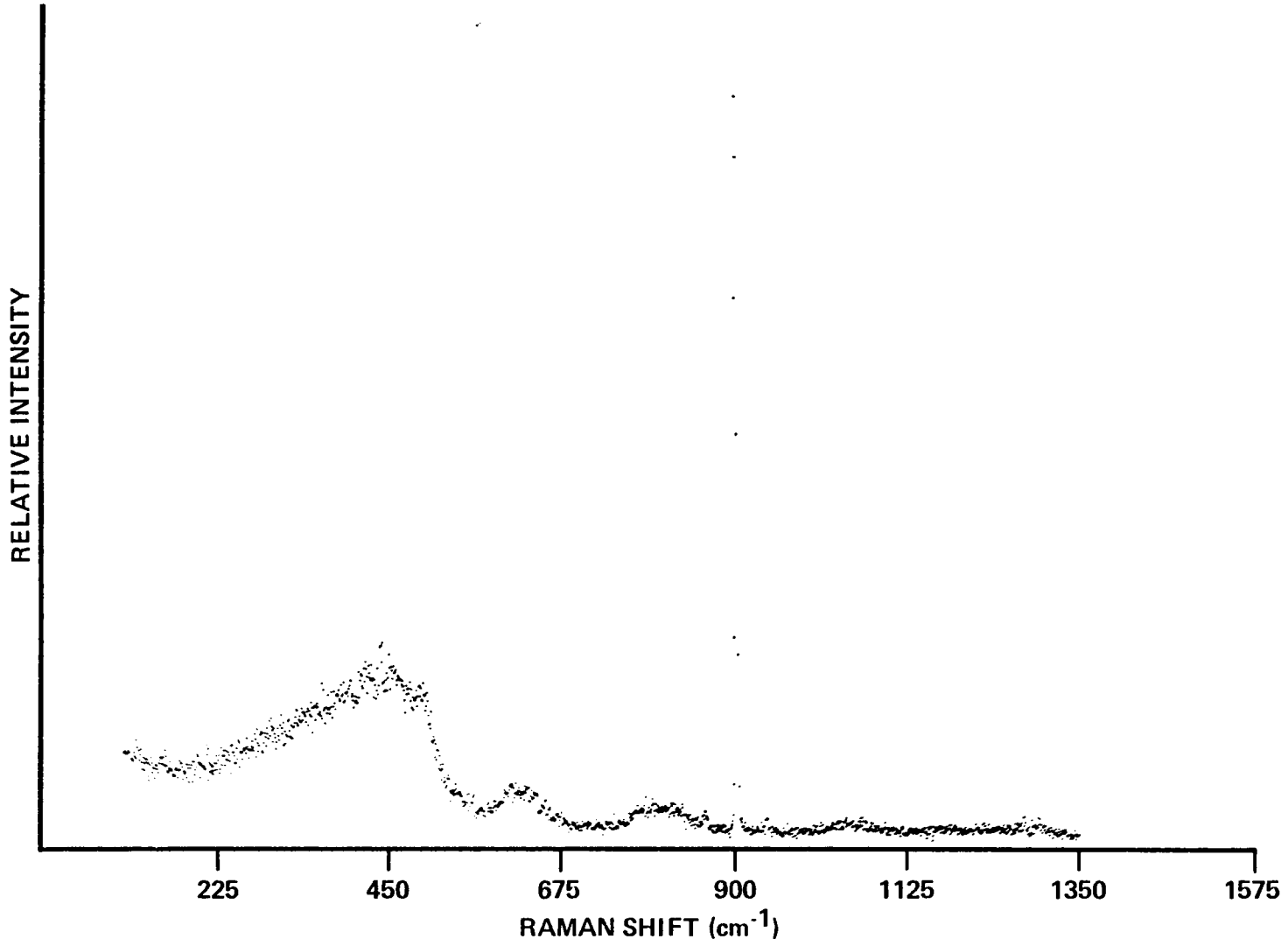


Figure 16. Raman spectrum of gaseous CF_4 at 298°K.

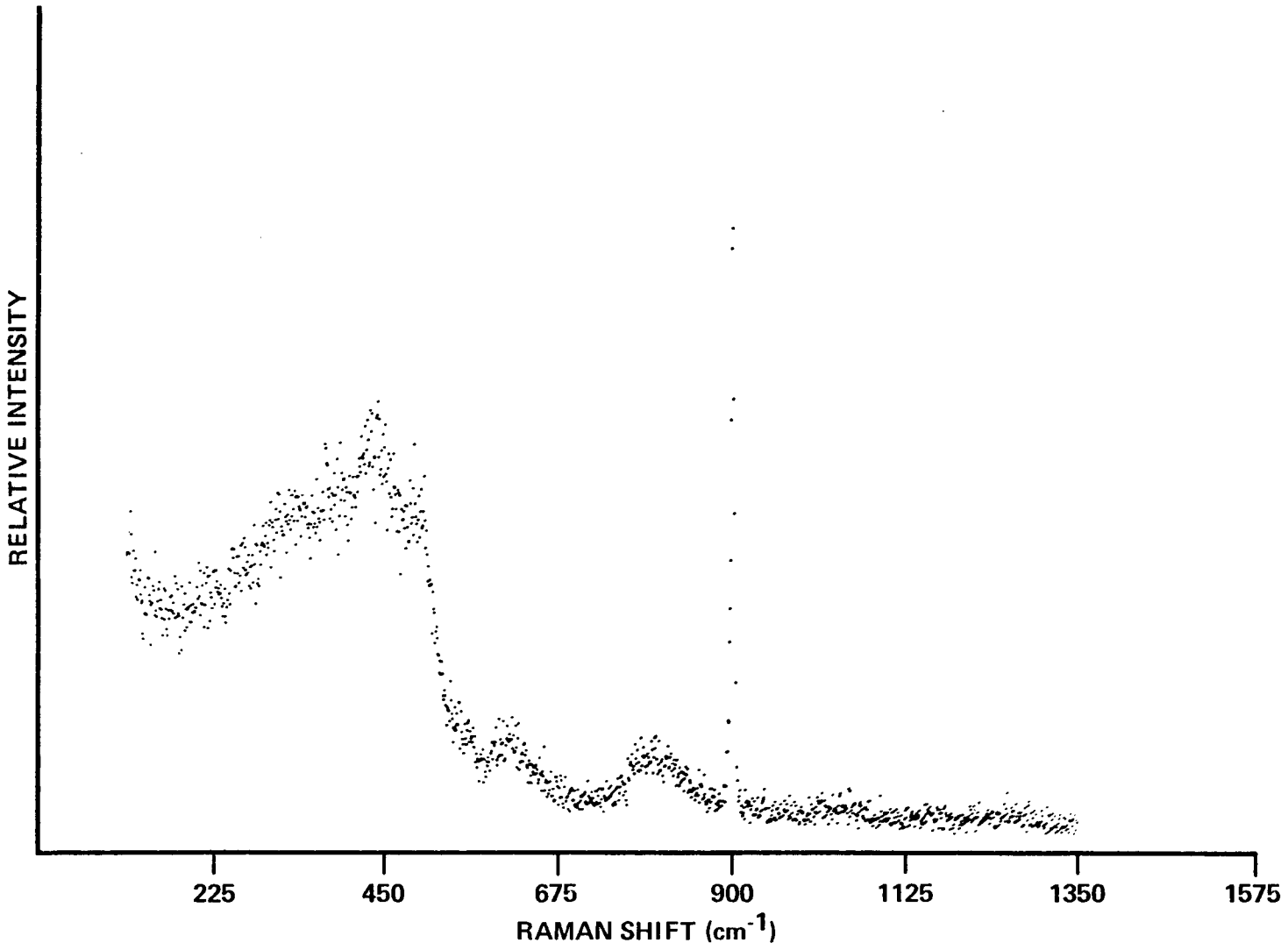


Figure 17. High temperature Raman spectrum of gaseous CF_4 at 593°K.

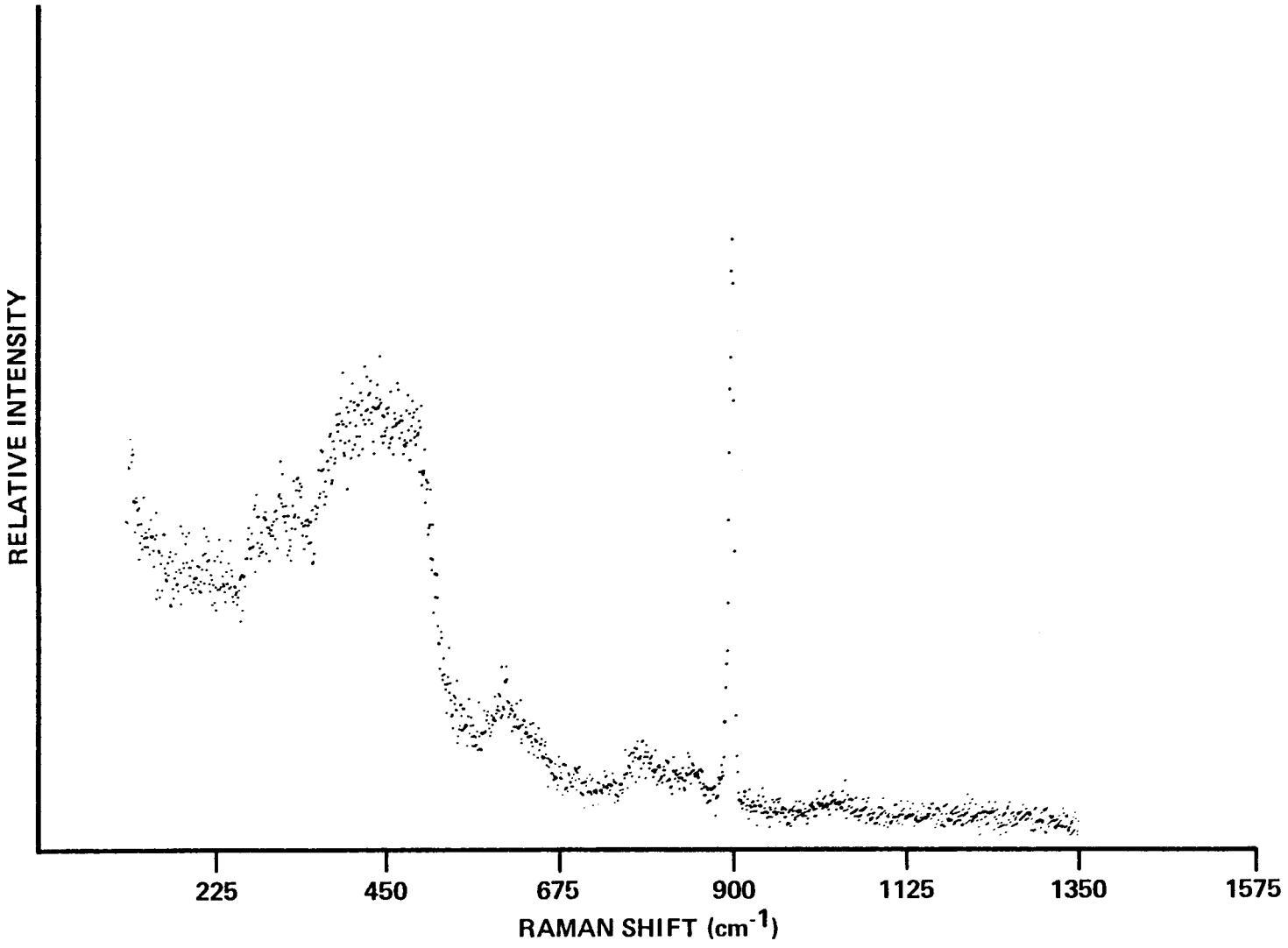


Figure 18. High temperature Raman spectrum of gaseous CF_4 at 774°K.

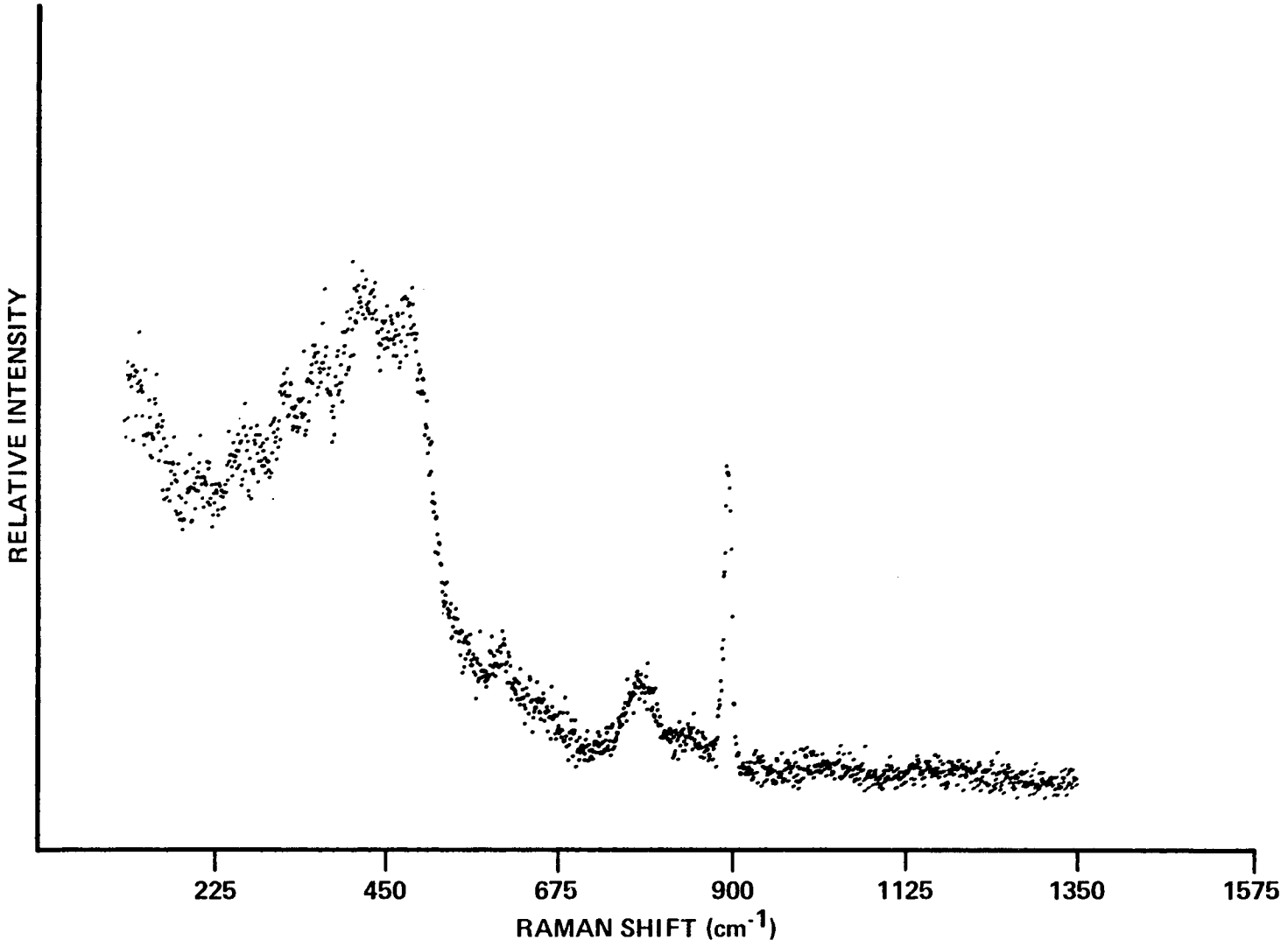


Figure 19. High temperature Raman spectrum of gaseous CF_4 at 983°K.

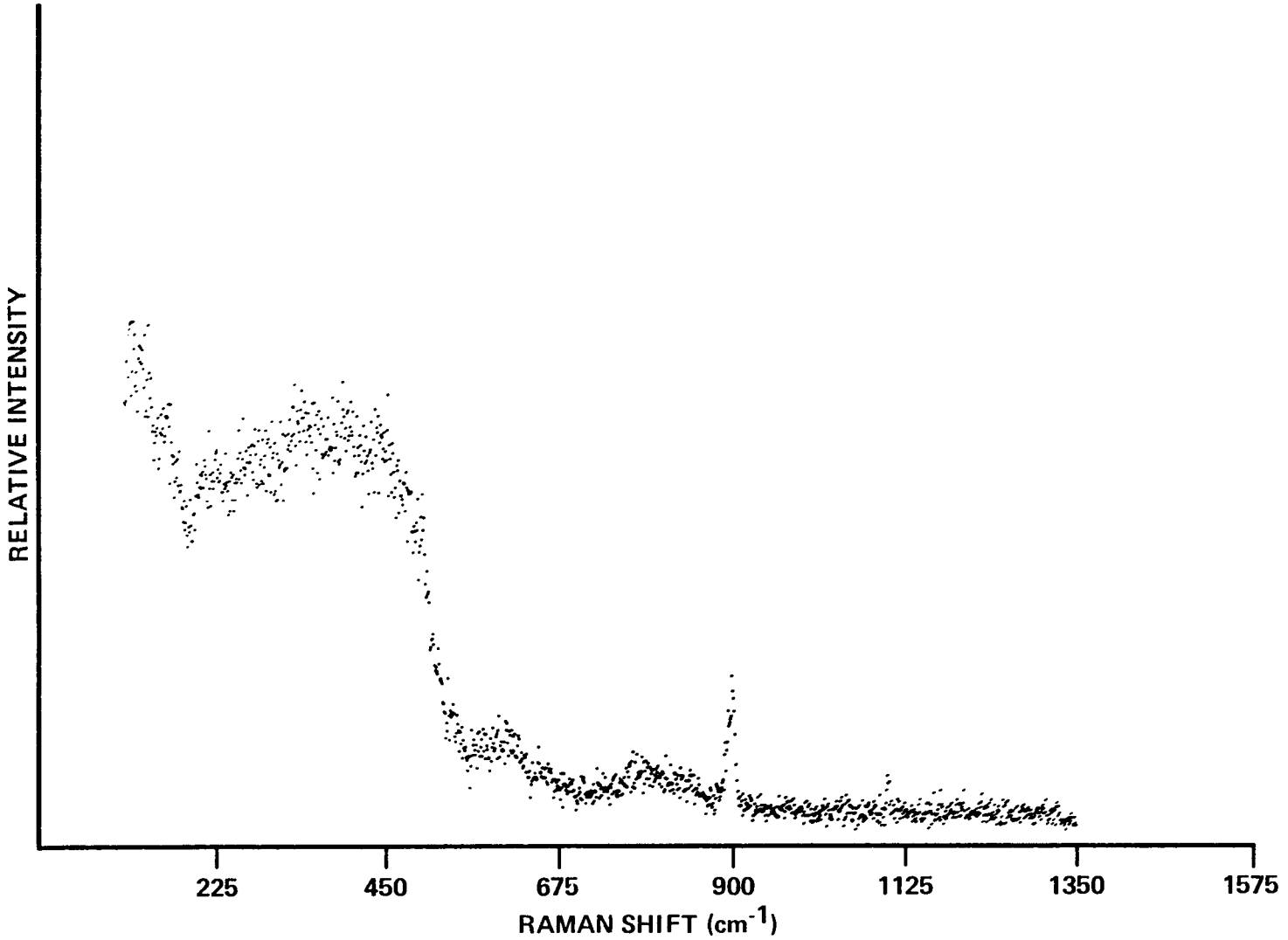


Figure 20. High temperature anti-Stokes Raman spectrum of gaseous CF_4 at 983°K.

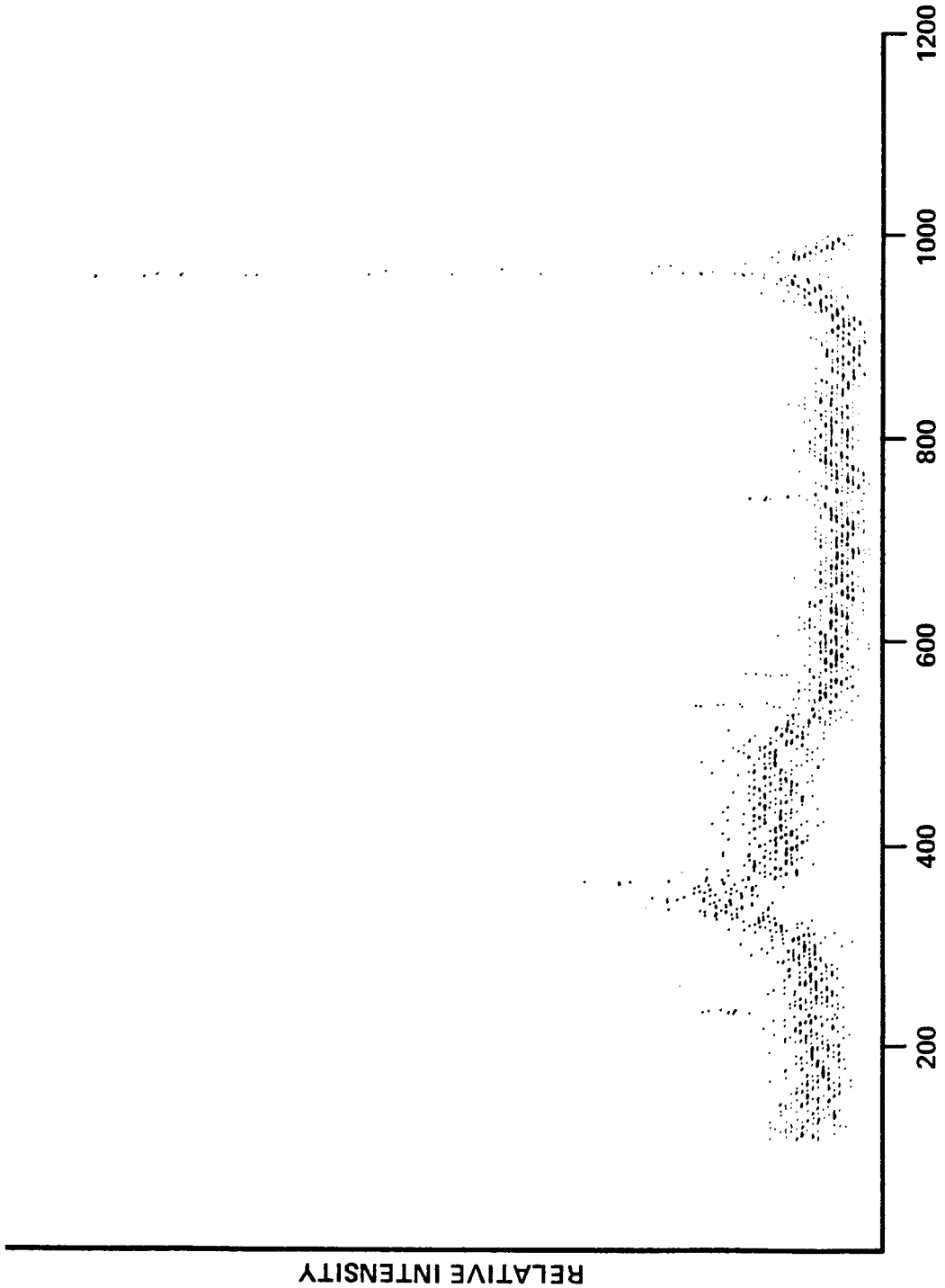


Figure 21. Raman spectrum of OsO_4 vapor at 340°K.

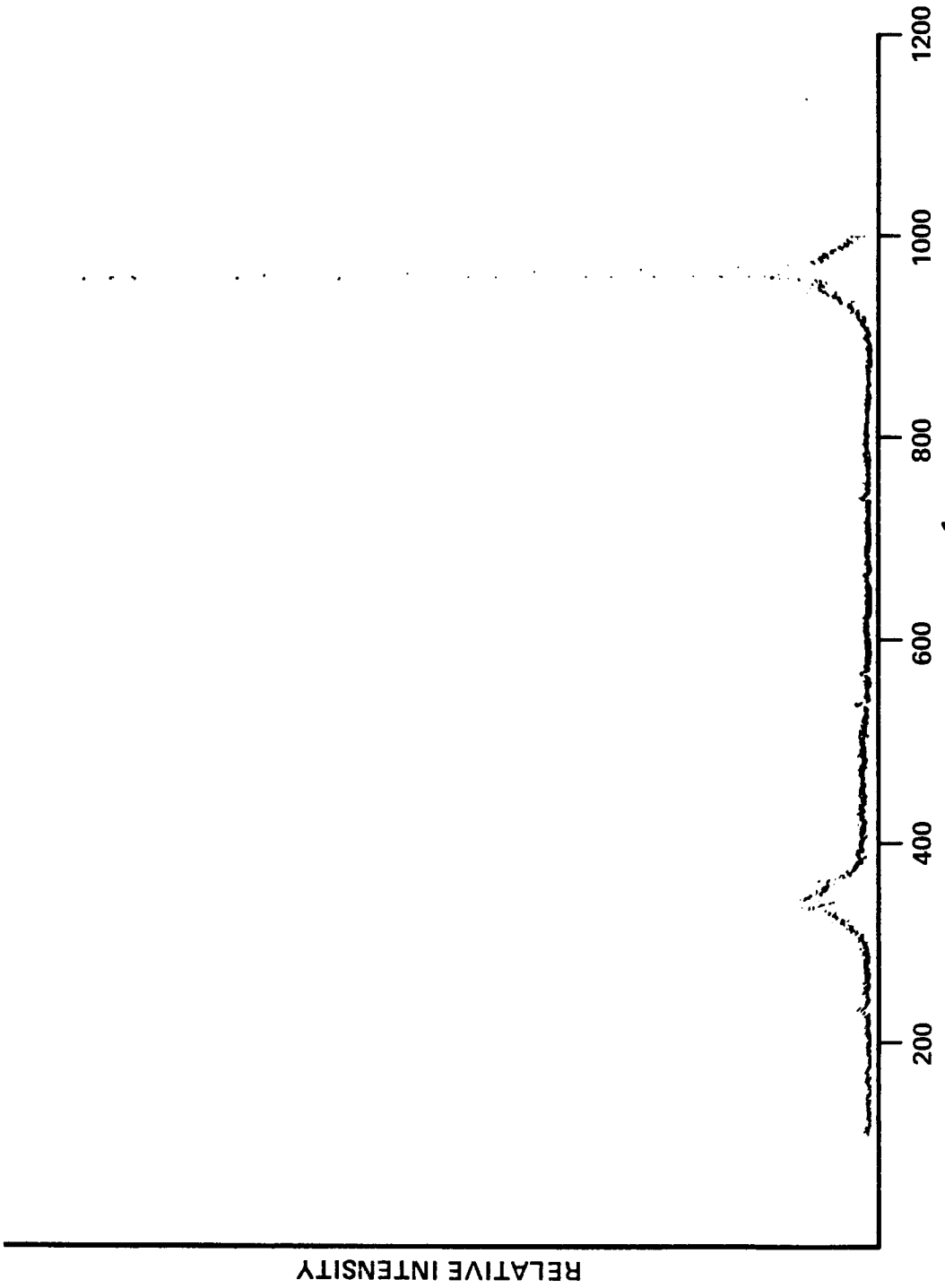


Figure 22. Raman spectrum of OsO_4 vapor at 398°K.

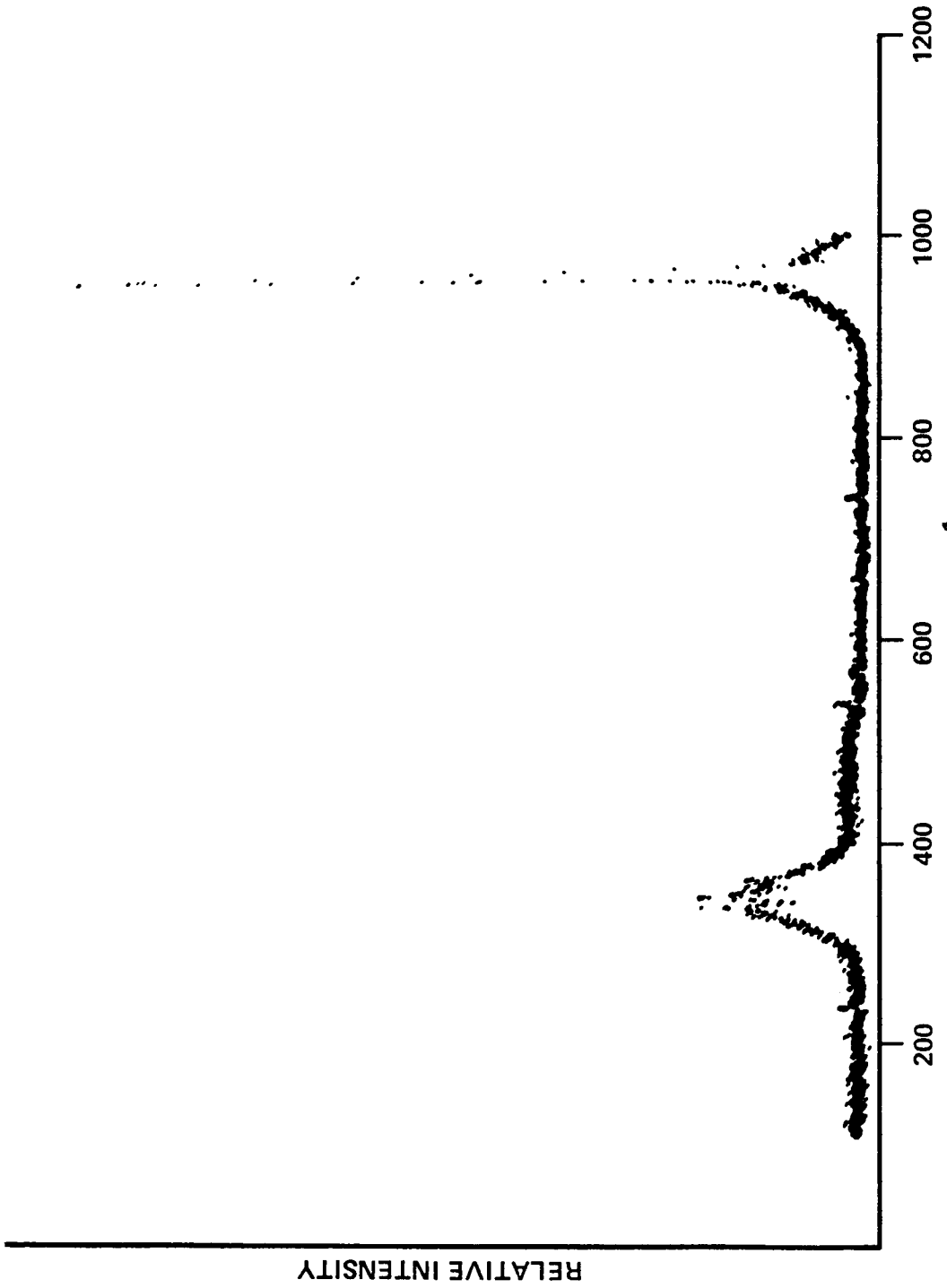


Figure 23. High temperature Raman spectrum of OsO_4 vapor at 626°K.

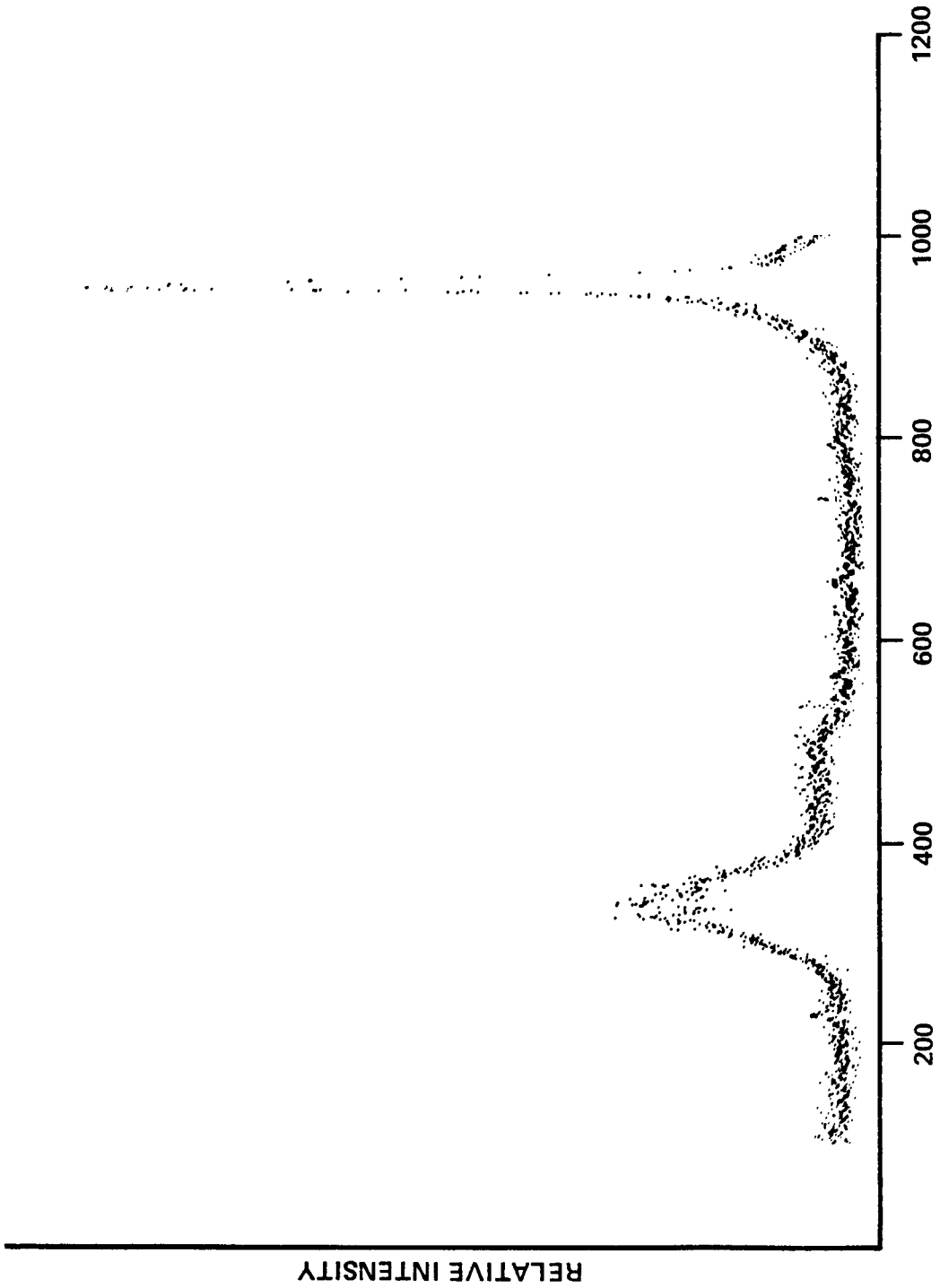


Figure 24. High temperature Raman spectrum of OsO_4 at 1038°K.

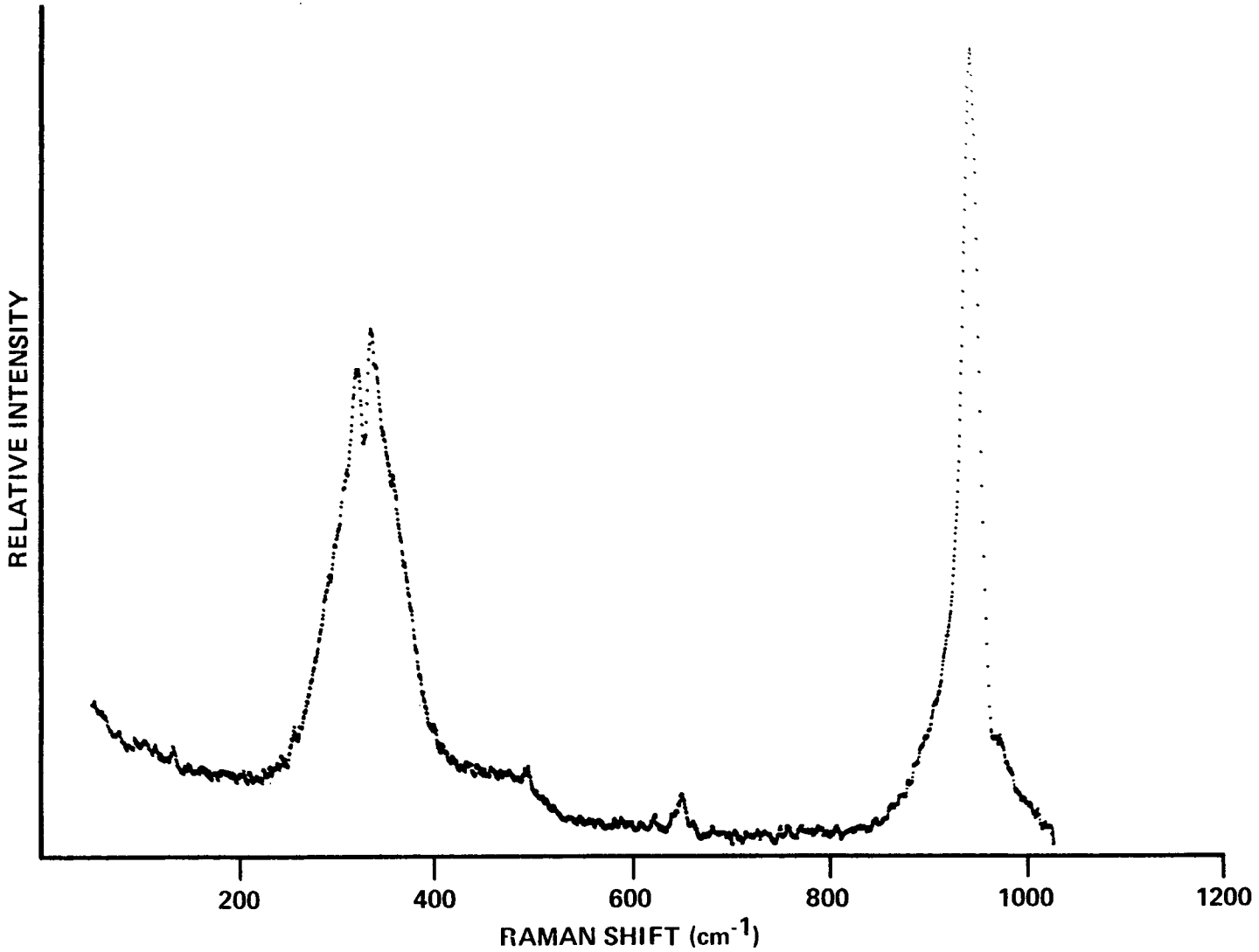


Figure 25. High temperature anti-Stokes Raman spectrum of OsO_4 vapor at 1268°K.

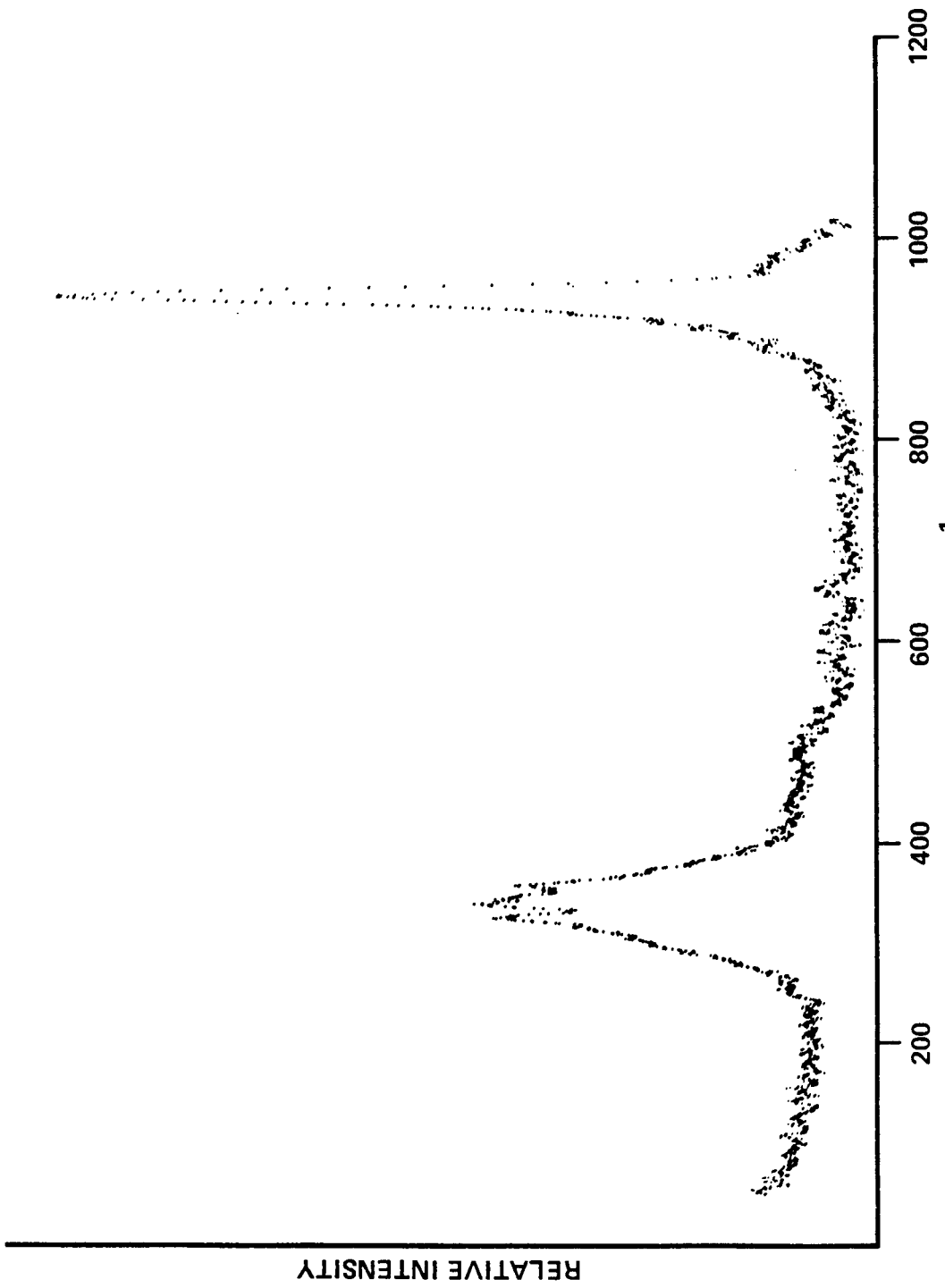


Figure 26. High temperature Raman spectrum of OsO_4 vapor at 1293°K.

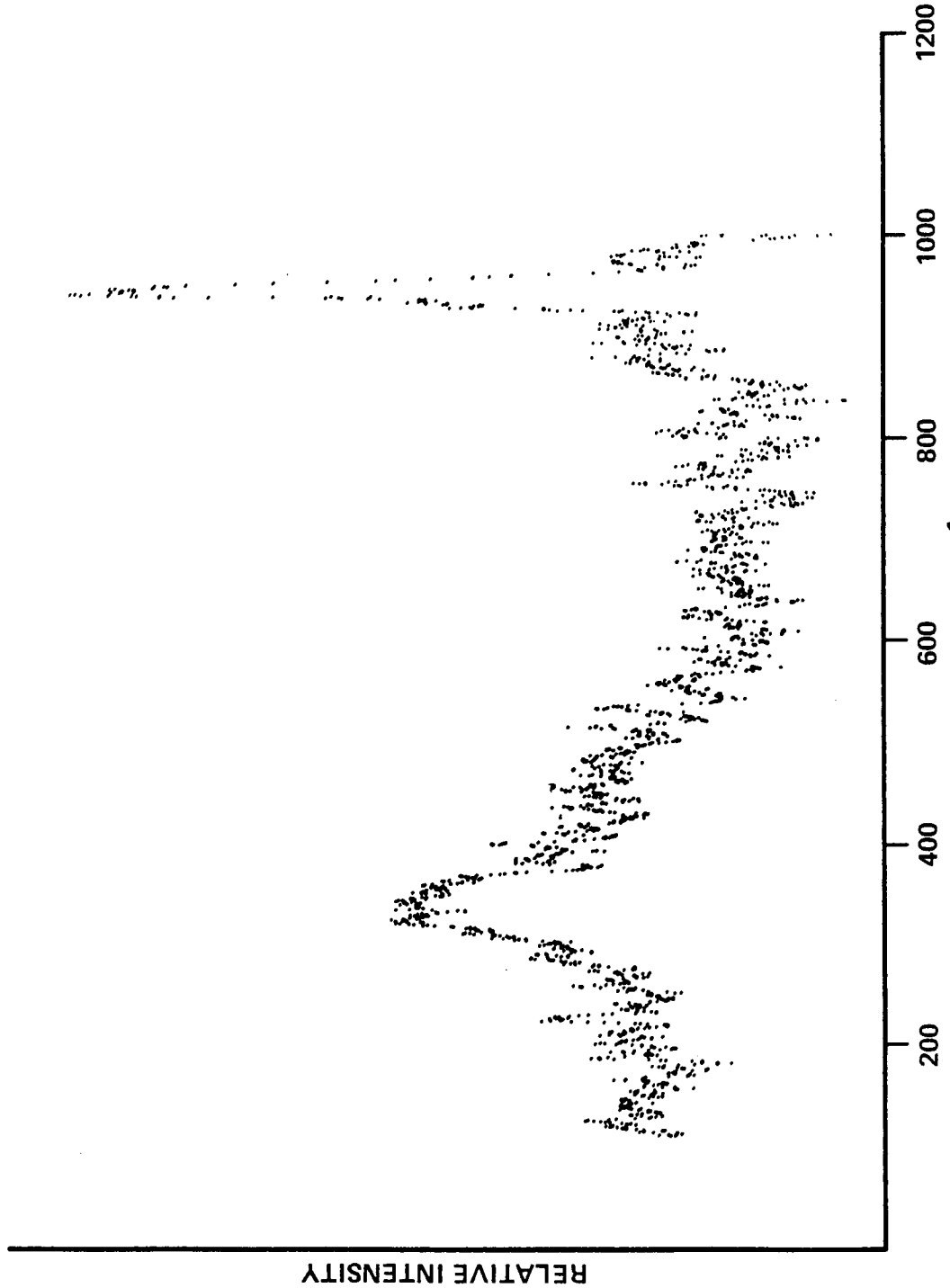


Figure 27. High temperature Raman spectrum of OsO_4 vapor at 1361°K and 0.2 watts laser power.

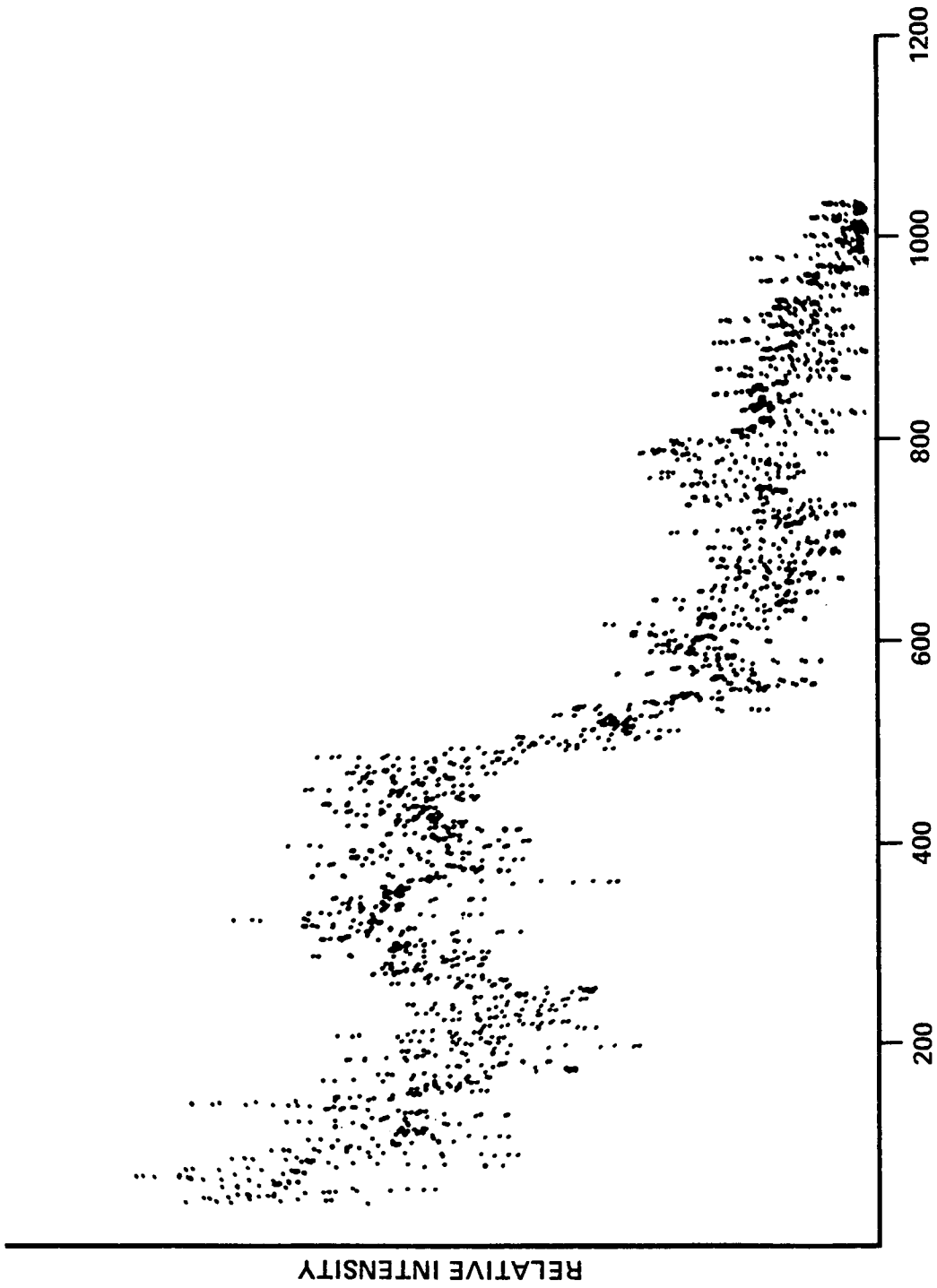


Figure 28. High temperature anti-Stokes Raman spectrum of $KReO_4$ vapor at 1343°K.

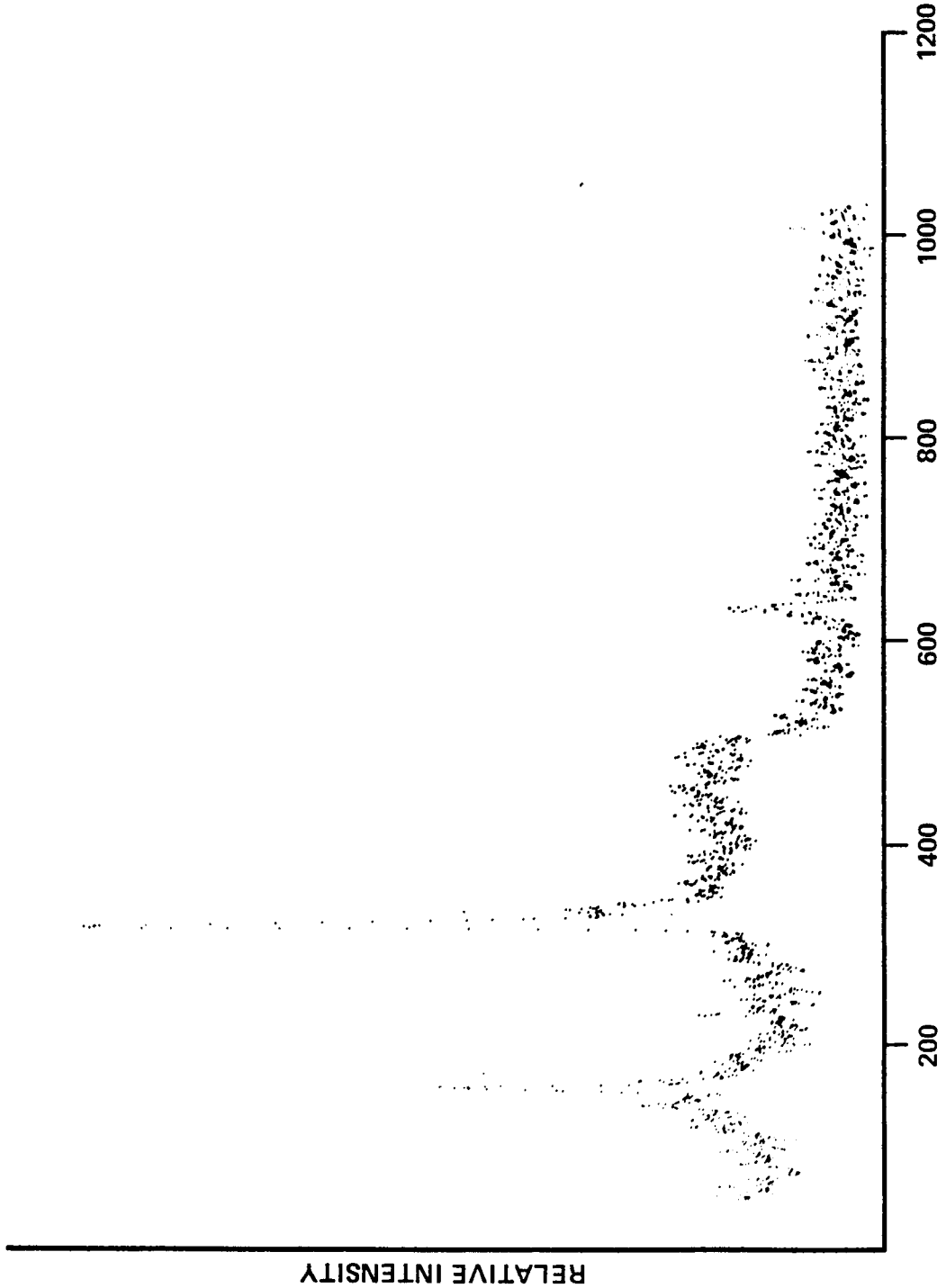


Figure 29. High temperature Raman spectrum of $KReO_4$ vapor at 1343°K.

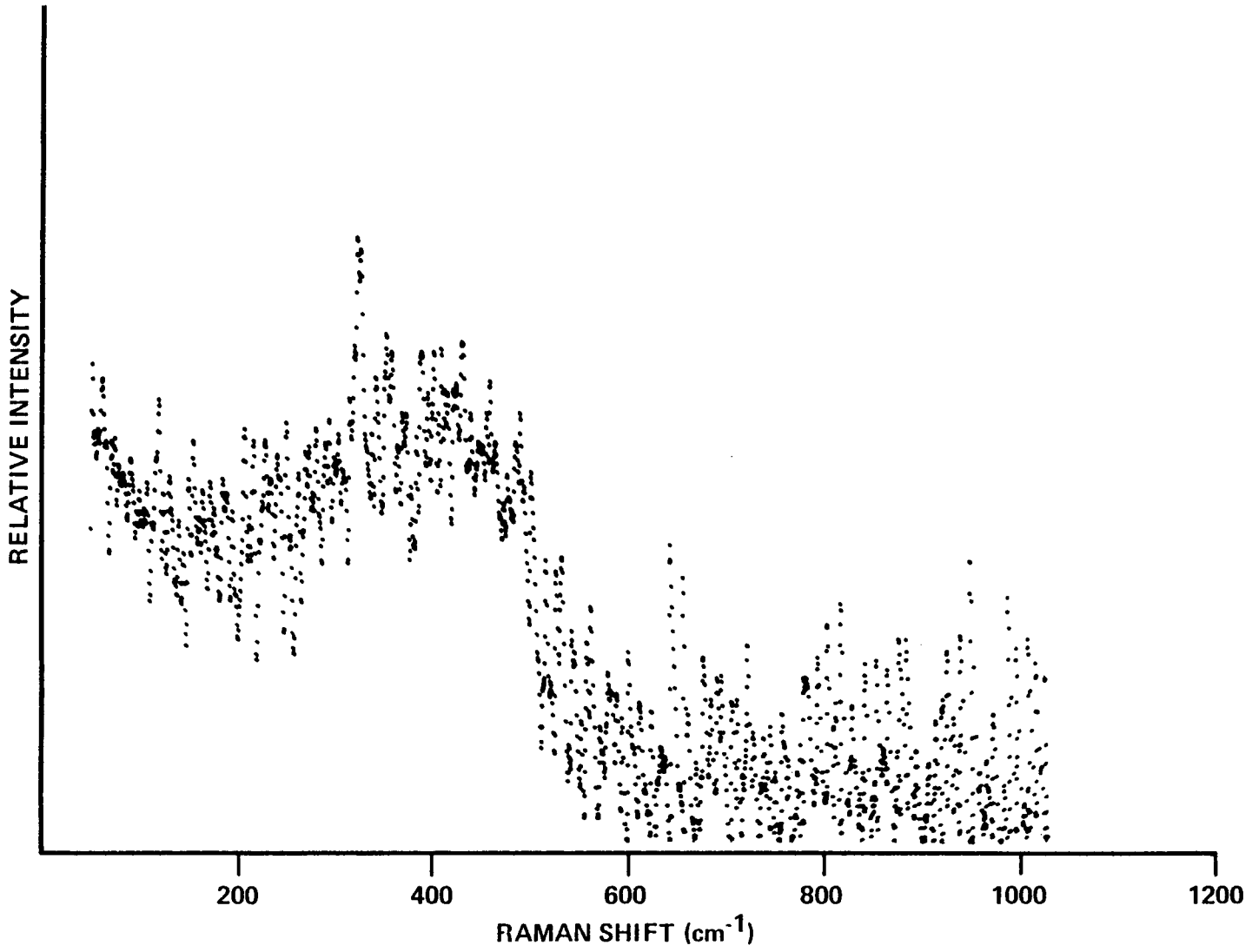


Figure 30. High temperature Raman spectrum of $RbReO_4$ vapor at 1336°K.

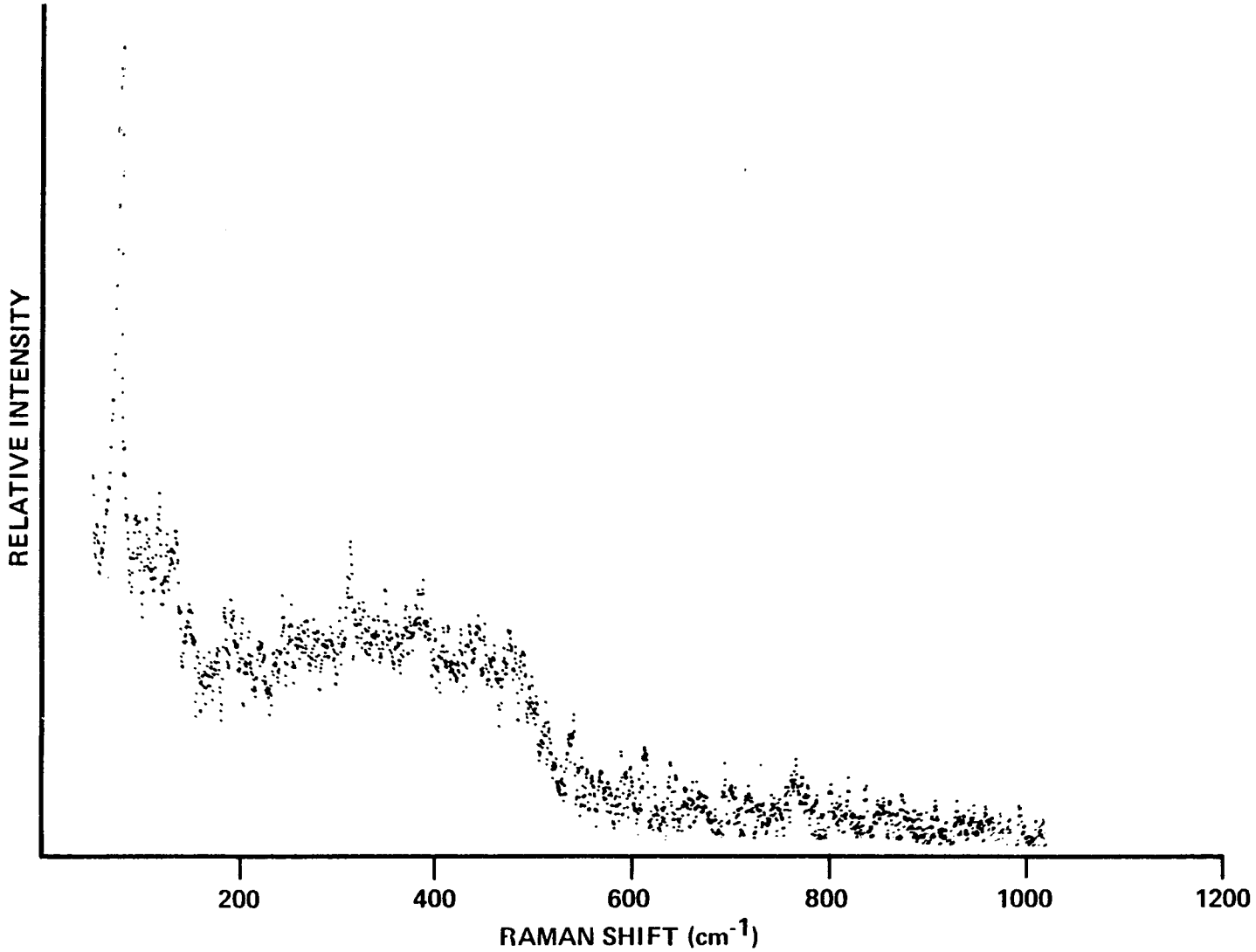


Figure 31. High temperature anti-Stokes Raman spectrum of $RbReO_4$ vapor at 1343°K.

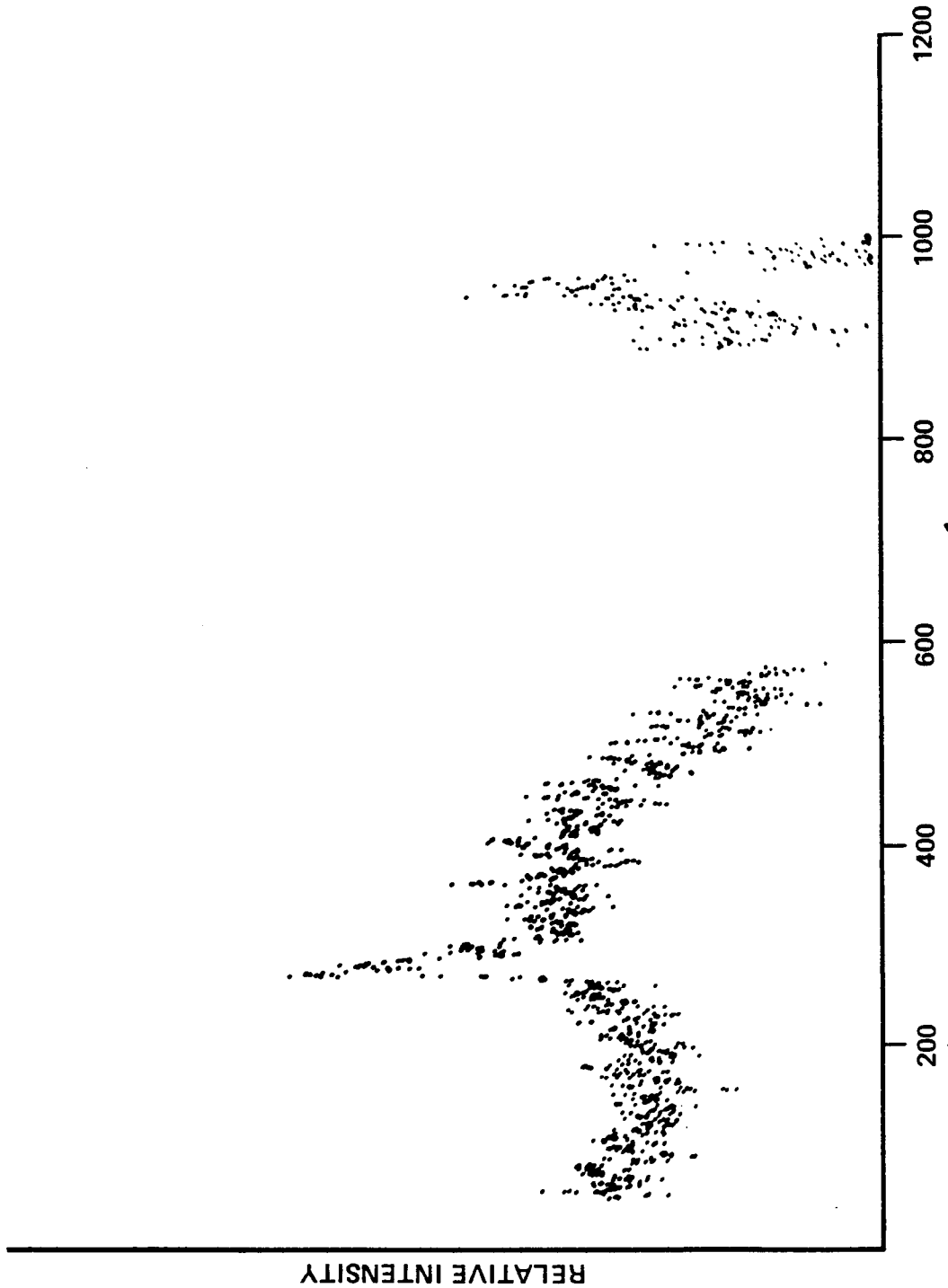


Figure 32. High temperature Raman spectrum of $CsReO_4$ vapor at 1400°K.

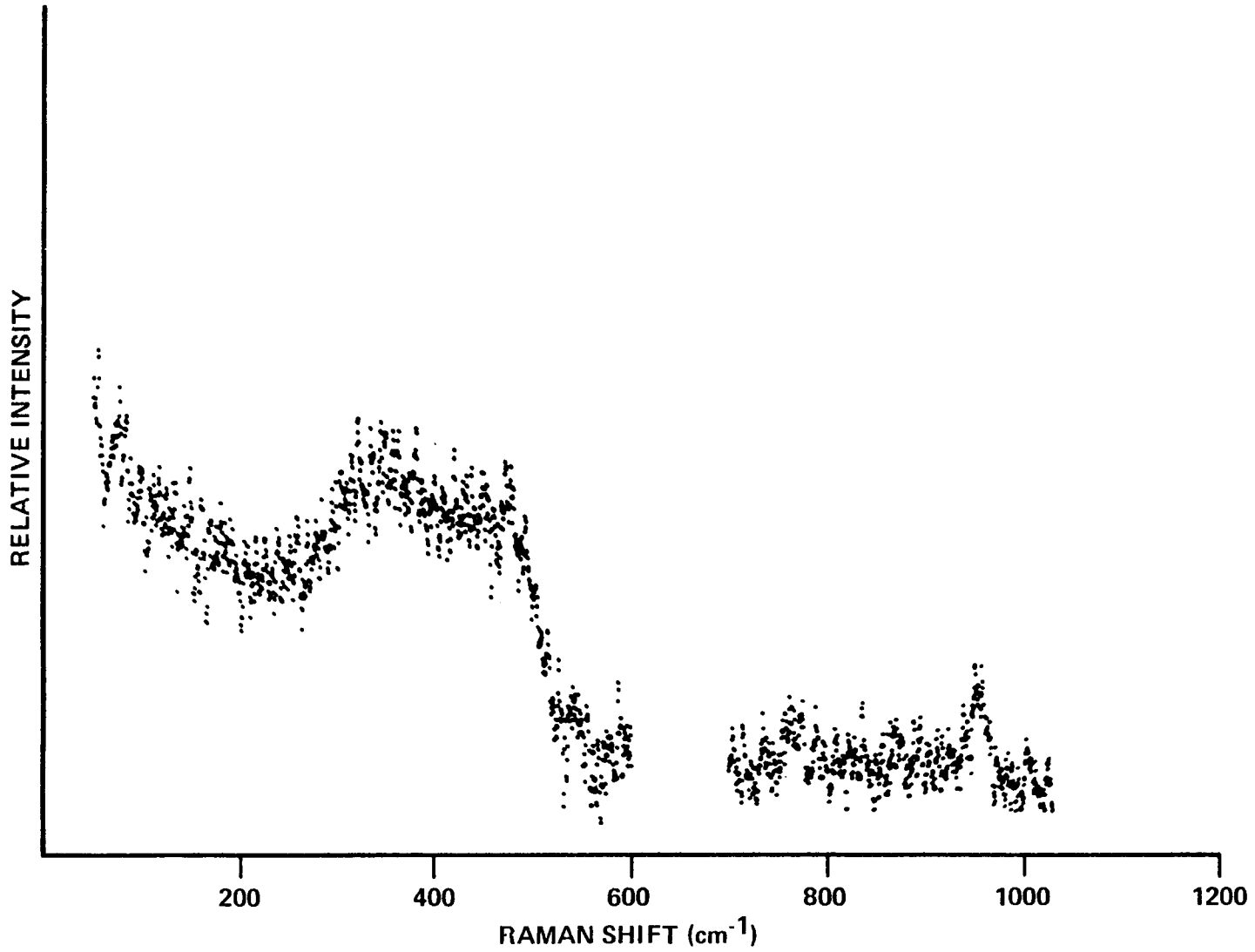


Figure 33. High temperature anti-Stokes Raman spectrum of $CsReO_4$ vapor at 1400°K.

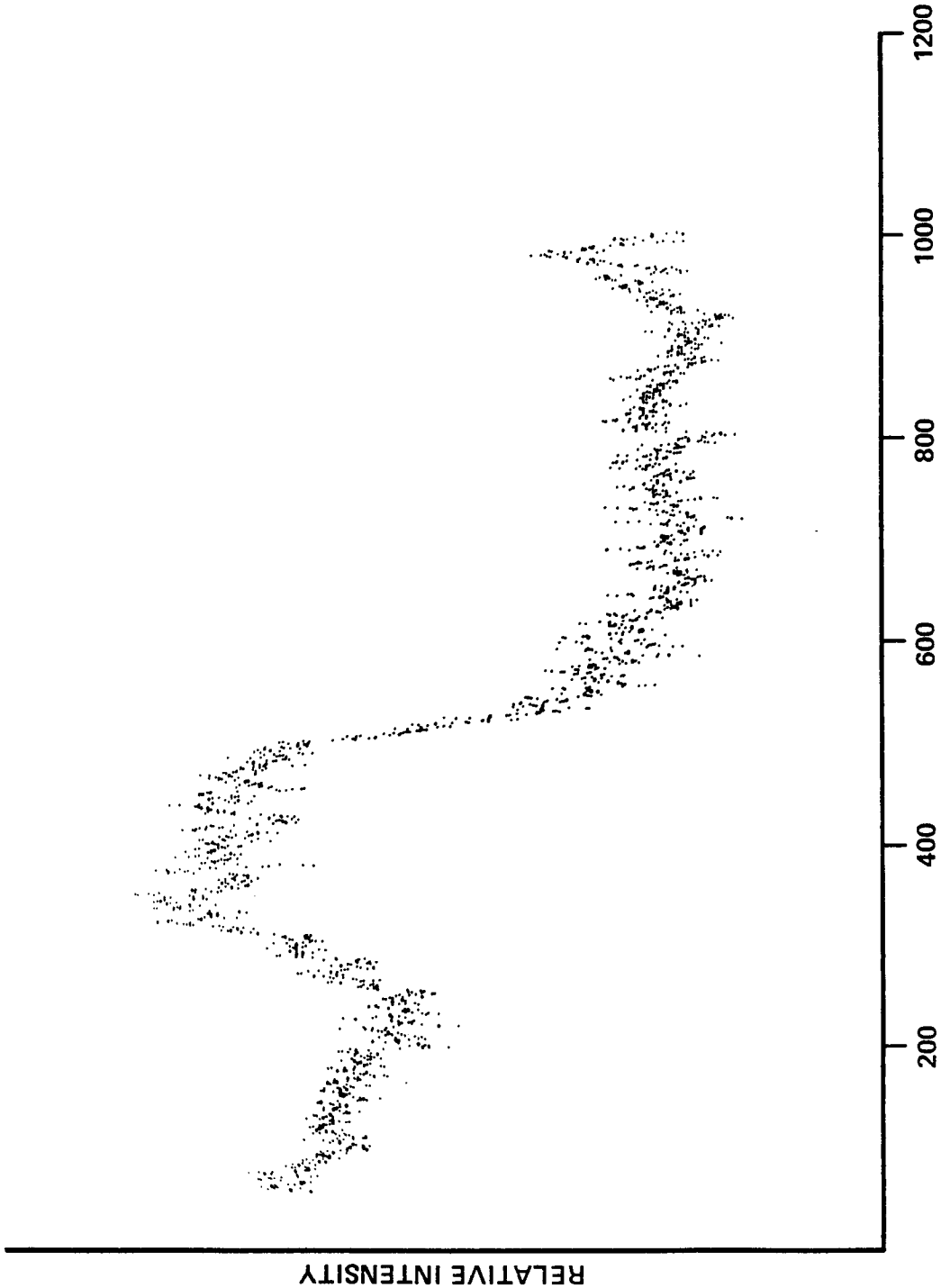


Figure 34. High temperature Raman spectrum of $TlReO_4$ vapor at 1233°K.

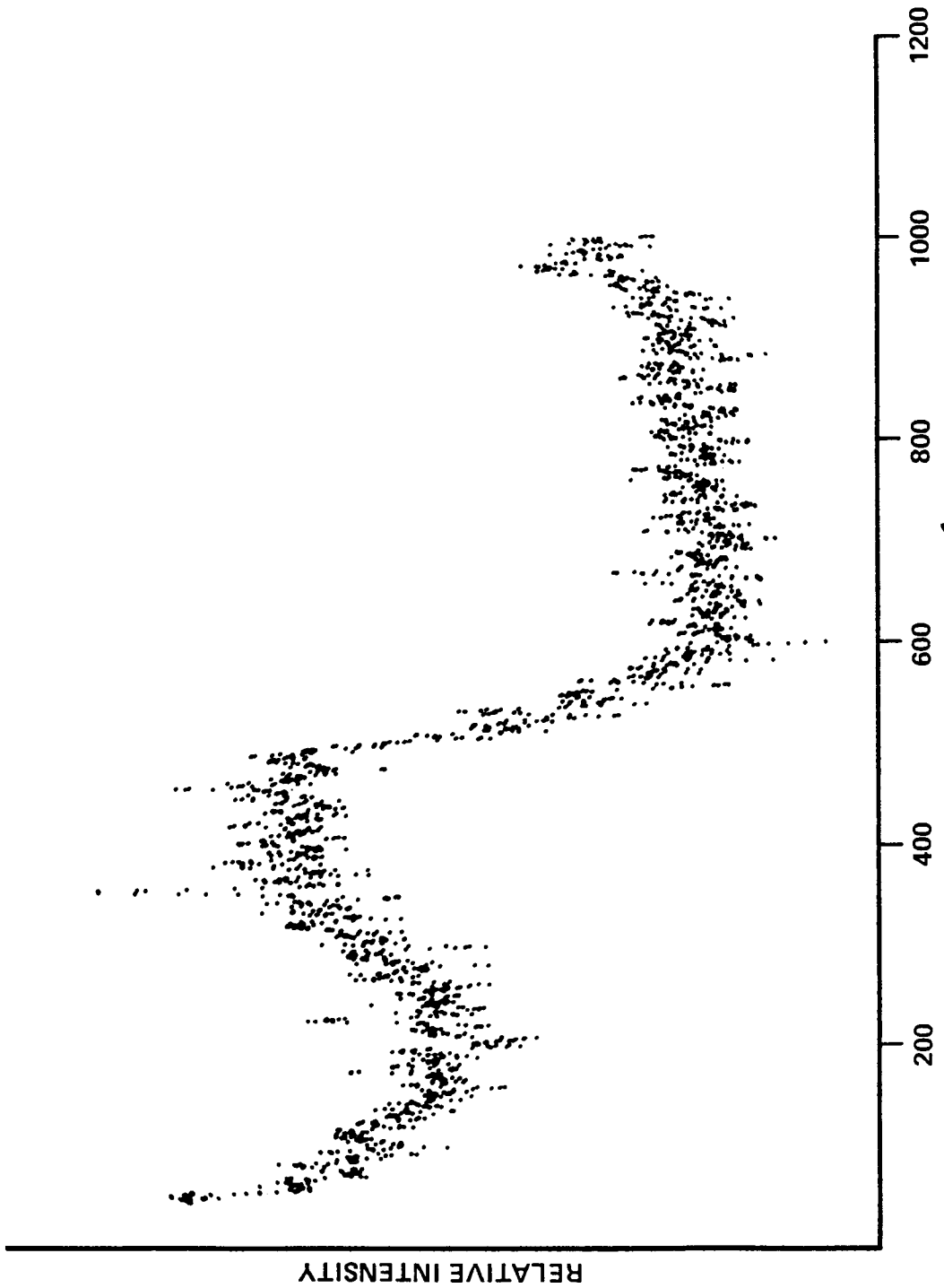


Figure 35. High temperature Raman spectrum of $TlReO_4$ vapor at 1413°K.

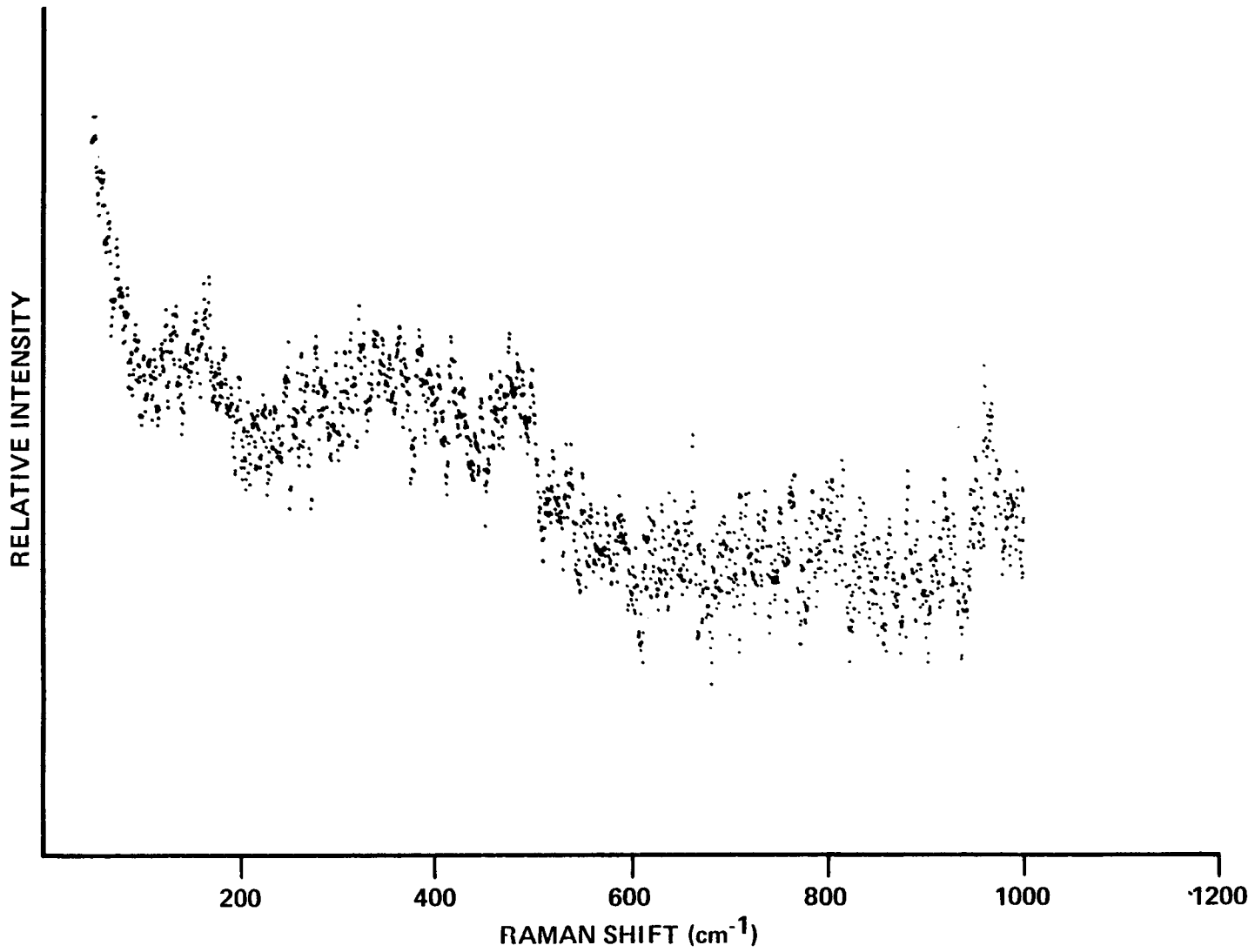


Figure 36. High temperature anti-Stokes Raman spectrum of $TlReO_4$ vapor at 1413°K.

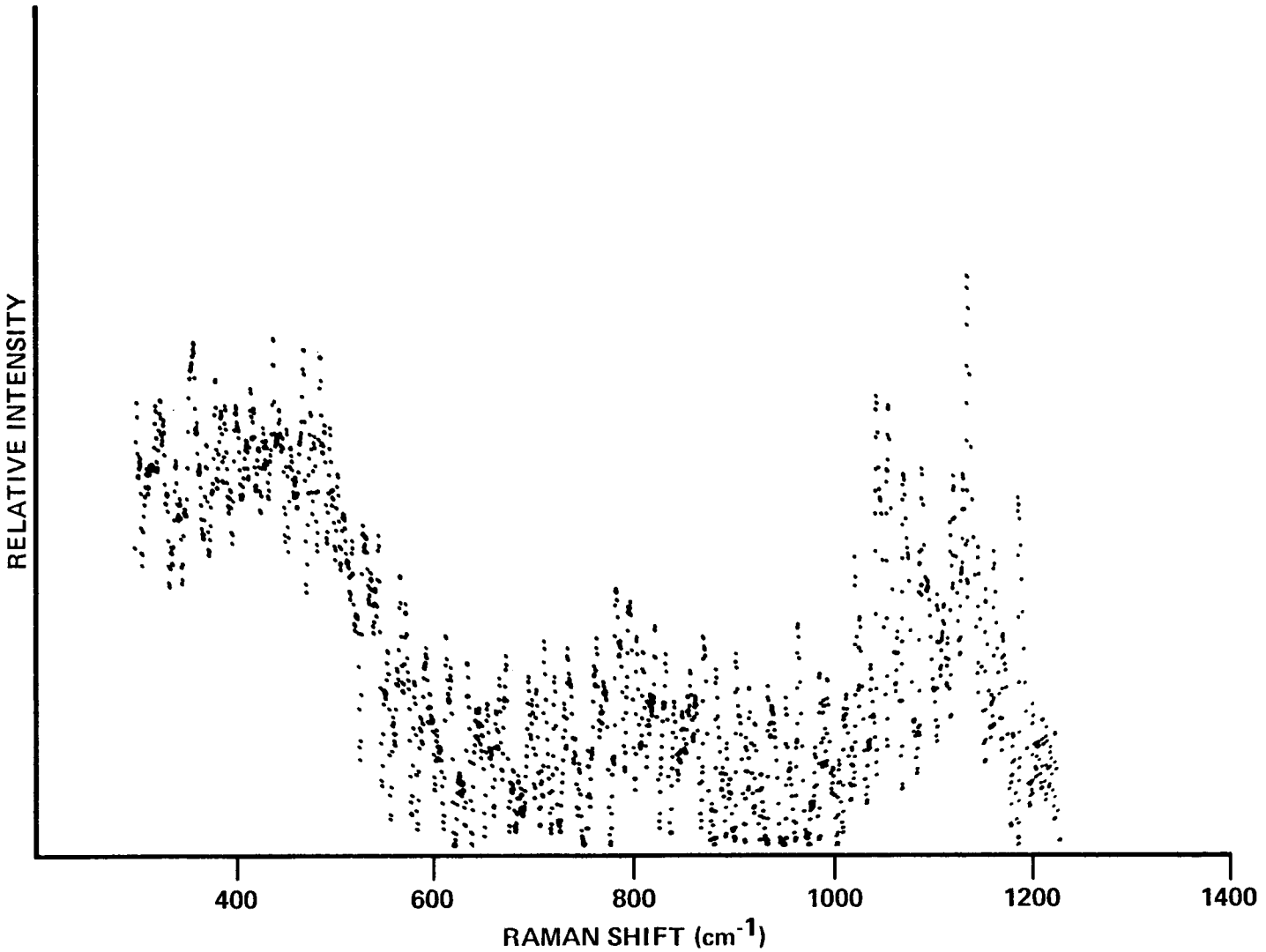


Figure 37. High temperature Raman spectrum of Cs_2SO_4 vapor at 1435°K.

TABLE II

INSTRUMENTAL AND SAMPLE PARAMETERS FOR CF_4 SPECTRA
Figures 16 through 20

Molecular density:	4×10^{18} molecules/cc
Laser power at sample:	3.5 watts, vertically polarized
Spectrometer resolution:	2.5 cm^{-1}
Electronic configuration:	Figure 11 (p 53)
Photomultiplier tube voltage:	800 V
Multichannel scalar parameters:	1.0 cm^{-1}/channel 3.25 sec/channel

TABLE III

INSTRUMENTAL AND SAMPLE PARAMETERS FOR OsO_4 SPECTRA

Figures 21 through 23	
Molecular density:	2×10^{19} molecules/cc
Laser power at sample:	3.5 watts, vertically polarized
Spectrometer resolution:	2.5 cm^{-1}
Electronic configuration:	Figure 11 (p 53)
Photomultiplier tube voltage:	800 V
Multichannel scaler parameters:	0.5 cm^{-1}/channel 3.5 cm^{-1}/channel
Figures 24 through 27	
Molecular density:	2×10^{19} molecules/cc
Laser power at sample:	2.0 watts, (except as noted) vertically polarized
Spectrometer resolution:	2.5 cm^{-1}
Electronic configuration:	Figure 12 (p 54)
Photomultiplier tube voltage:	800 V
Bandpass mode, 100% Q	
30 sec integration time	
Multichannel scaler parameters:	0.5 cm^{-1}/channel 8.5 sec/channel

TABLE IV

INSTRUMENTAL AND SAMPLE PARAMETERS FOR $MReO_4$ (M = K, Rb, Cs, Tl) AND Cs_2SO_4 SPECTRA
Figures 28 through 37

Molecular density:	1×10^{18} molecules/cc
Laser power at sample:	2 watts, vertically polarized
Spectrometer resolution:	2.5 cm^{-1}
Electronic configuration:	Figure 12 (p 54)
Photomultiplier tube voltage:	800 V
Bandpass mode	100% Q
	30 sec integration time
Multichannel scaler parameters:	0.5 cm^{-1}/channel
	8.5 sec/channel

additional bands in the Stokes spectrum, run after the anti-Stokes, is probably indicative of decomposition products. A slight yellowing of the sample was also noted as well as dark regions on the cell wall where the excitation beam passed through the cell. This latter phenomenon was also experienced with Re_2O_7 which is apparently photolytically unstable to 488.0 nm radiation.

The sulfates proved extremely troublesome. In order to obtain sufficient vapor pressure the furnace had to be run near its limit at 1500°K. But in this temperature region the sulfates became corrosive to silica and the cell appears to devitrify. The extent of the attack can be seen in Figure 38 (p 90) where a normal cell containing $KReO_4$ is on the left and the devitrified cell containing Cs_2SO_4 is on the right. The corrosive attack is apparently unique to the sulfates since several of the perrhenates were run in the same temperature region and the cell appeared unaffected. One sample of Cs_2SO_4 survived long enough to obtain the spectrum in Figure 37 (p 85). A sample of Tl_2SO_4 could not be maintained long enough to obtain any reliable spectrum.

As a final check on the compound stabilities, the cells were broken open after completion of the spectral run and a sample of condensate analyzed by X-ray powder diffraction by Mr. P. W. Pickrell of Union Carbide Corporation, Nuclear Division. The powder patterns are shown in Figure 39 (pp 91-93). All, with the exception of $TlReO_4$, were compared to standard reference data in the "Powder Diffraction File-Inorganic" and verified as being the starting materials.[330] The $TlReO_4$ was not listed so a standard pattern of the starting material was prepared for

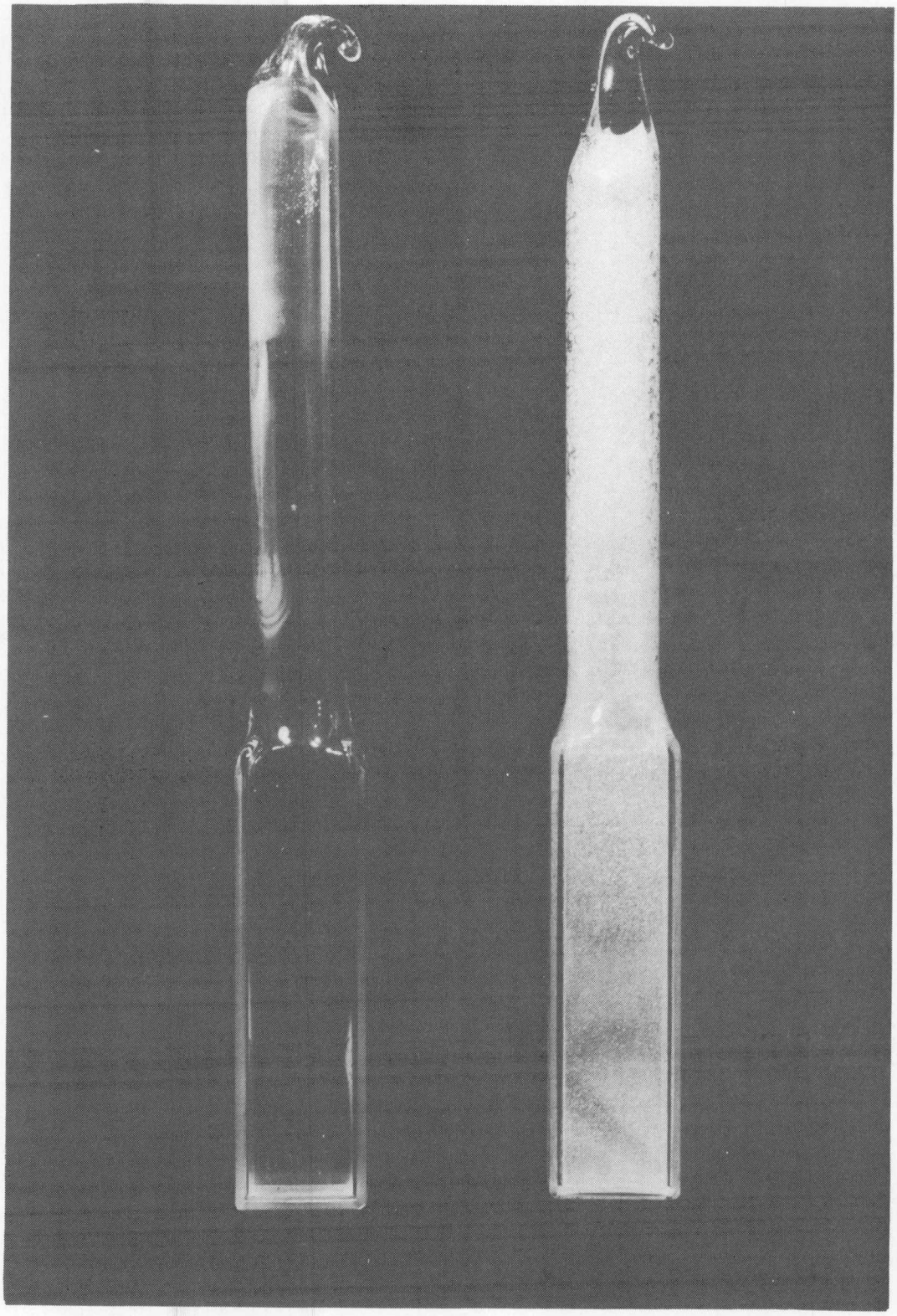


Figure 38. Photograph showing normal cell after use on the left and devitrified cell containing Cs_2SO_4 on the right.

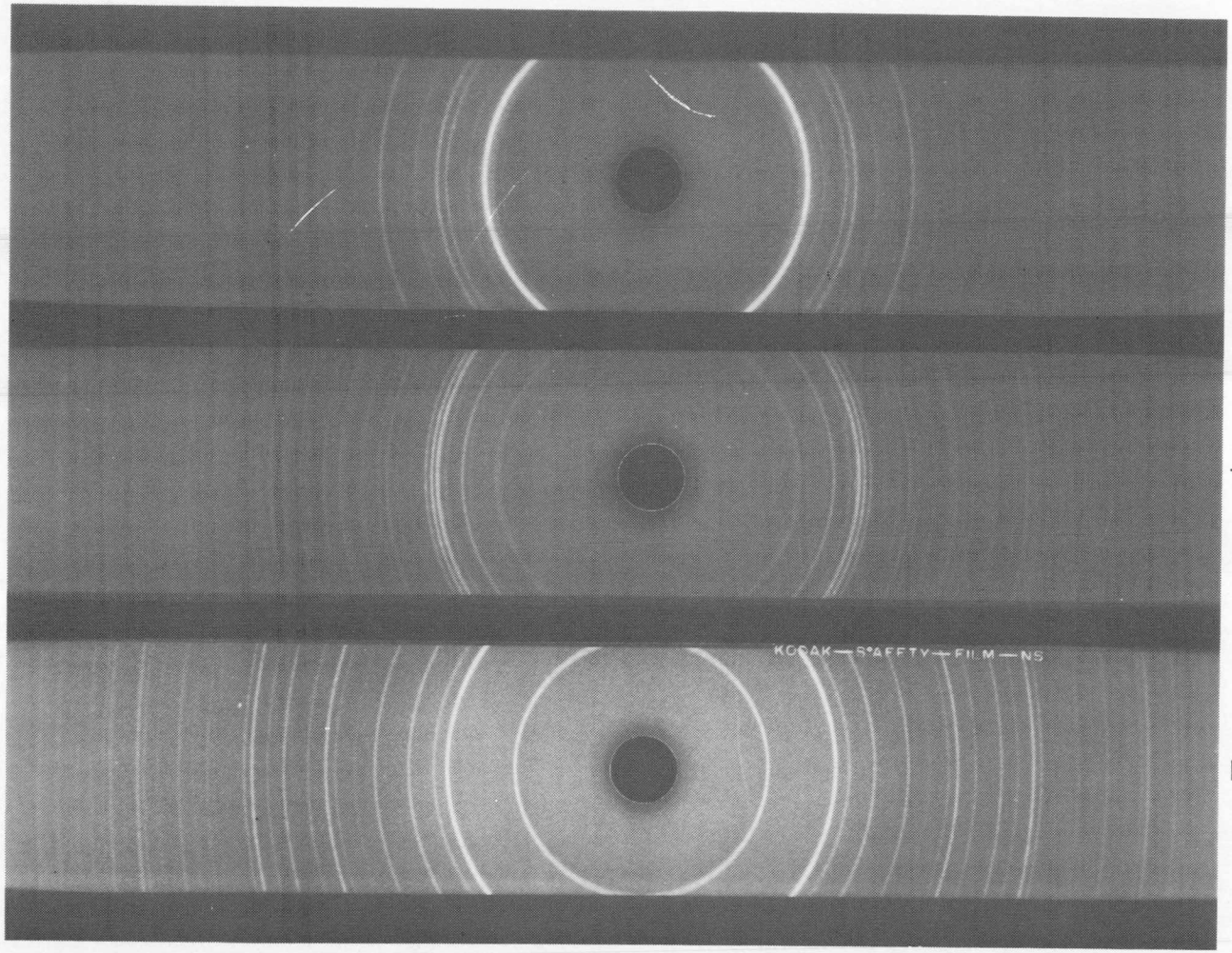


Figure 39. X-ray powder diffraction patterns of compounds removed from cells after high temperature vapor studies.

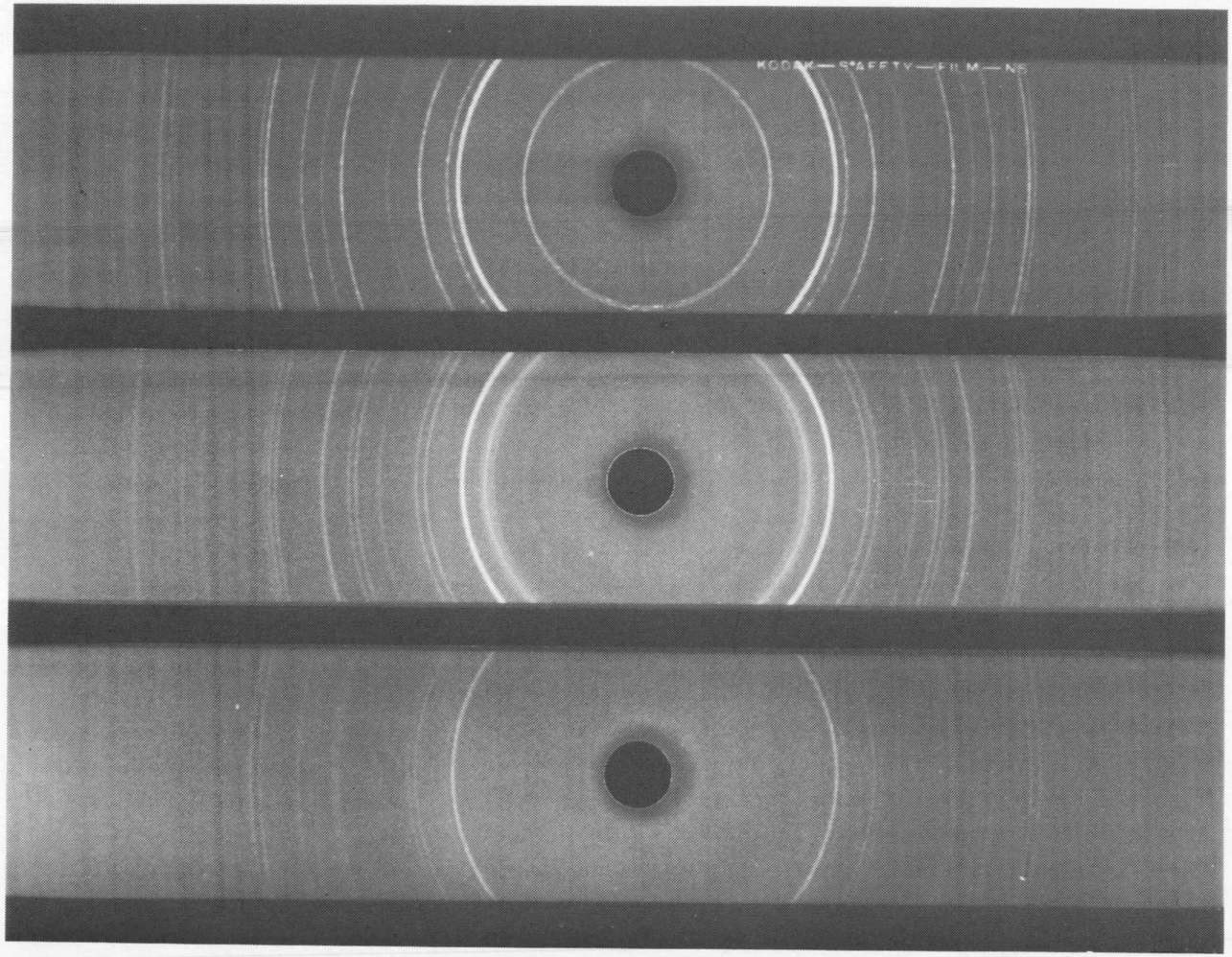
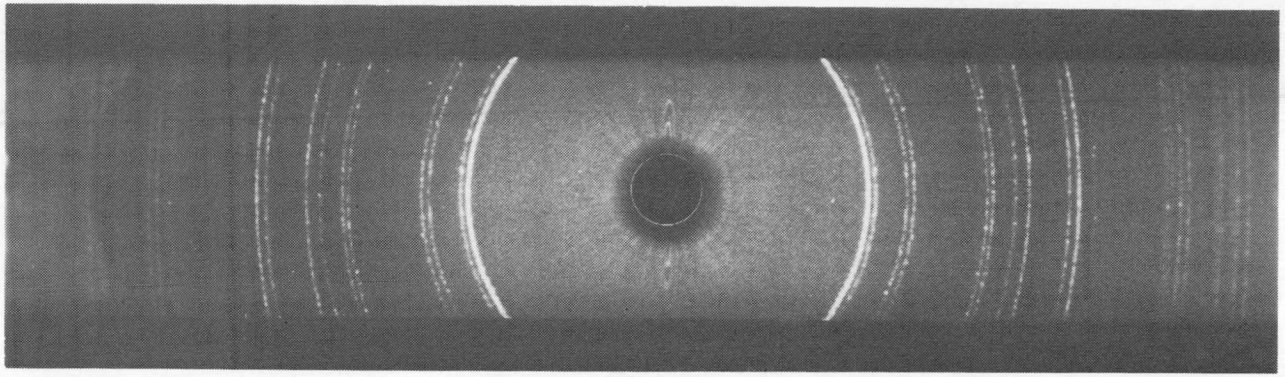


Figure 39. (Continued)



$TlReO_4$ standard

Figure 39. (Continued)

comparison and a match was obtained. There is a strong indication of SiO_2 in the sulfates and a much weaker indication in the $CsReO_4$. Surprisingly, the sulfates and the $KReO_4$ showed no evidence of decomposition in the powder patterns.

CHAPTER V

CONCLUSION

One of the major aims of this study was to evaluate the utility of Raman spectroscopy as a technique for structure determination of high temperature vapors. A special Raman spectrometer and furnace were constructed and, through the use of phase sensitive detection, spectra of gases and vapors at temperatures to 1500°K have routinely been obtained. The 1500°K does not appear to be an upper limit although at higher temperatures problems with materials of construction would rapidly become severe. The use of sapphire sample cells may overcome the problem of corrosive attack by the vapor and certainly would extend the temperature range before the cell failed. Improvement in the sensitivity is mainly a problem in improving the Raman scattering signal to noise ratio. Higher laser power, shorter excitation wavelength, and higher molecular density of the sample vapor, separately or in combination, would increase the Raman signal. Also operating at a shorter excitation wavelength would reduce the background from black body radiation or allow higher temperature operation at an equivalent background level to that presently experienced.

In Table I (pp 4-11) a large number of ionic ternary compounds are indicated to be stable in the vapor phase. Included in this list are the alkali metal and thallium nitrates; but in all the instrumental methods involving the vapor phase, the residence time in the measurement region of a given volume of vapor is short. This author's experience

with $TlNO_3$ and $CsNO_3$ was that they were almost completely decomposed during a spectral run. In the Raman system the $TlNO_3$ and $CsNO_3$ vapors were in a static high temperature condition for a period of several hours. These results have lead to the following conclusion which should be considered if investigations of other ionic ternary compounds are performed. The decomposition of these compounds is slow on a scale of the residence time of the vapor in the analyzing region of an instrument such as a mass spectrometer or photoelectron spectrometer. A dynamic condition exists for the vapor. If decomposition does occur, it apparently happens outside of the analyzing region, and the decomposition products are pumped away. In the Raman system with a static vapor, an equilibrium condition can be approached. If the equilibrium lies strongly toward decomposition at the temperature of the measurement, then a clean spectrum of the initial compound may not be obtainable. This conclusion is supported by the spectra of $KReO_4$ [Figures 28 and 29 (pp 76-77). The anti-Stokes spectrum of $KReO_4$ [Figure 28 (p 76)] was run first and resembles the anti-Stokes spectra of the other perrhenates. By the time the Stokes spectrum was run, the sample had been at 1413°K for four to five hours; and as can be seen in Figure 29 (p 77), the decomposition products had begun to dominate the spectrum.

A comparison of the CF_4 spectra [Figures 16 through 20 (pp 64-68)] as a function of temperature at constant molecular density is instructive in the way the different vibrational modes respond. Carbon tetrafluoride, having T_d symmetry, has four normal vibrational modes: a singly degenerate symmetric stretch ν_1 at 908 cm^{-1}, a doubly degenerate

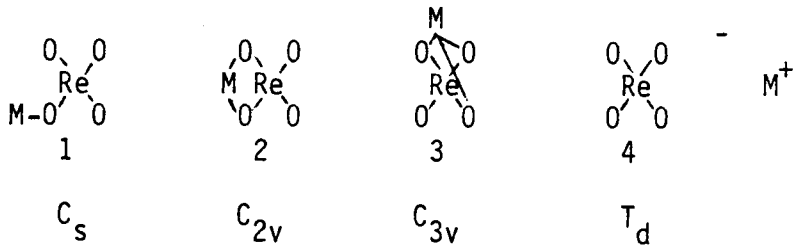
bending mode ν_2 at 435 cm^{-1}, a triply degenerate ν_3 at 1260 cm^{-1}, and a triply degenerate bending mode ν_4 at 631 cm^{-1}. The ν_3 vibration is not apparent in any of the spectra, the ν_1 vibration has a threefold increase in peak width and a halving of the relative intensity on raising the temperature from 298°K to 983°K, and the low frequency bending mode (ν_2) is a very broad band and experiences an almost four-fold increase in relative intensity over the same temperature range. The FWHM bandbreadth for ν_2 is only slightly increased over the 685°K temperature range. The ratio of peak heights ν_2 to ν_1 ranges from 0.23 at 298°K to 0.98 at 983°K.

A similar comparison of the OsO_4 spectra is equally instructive. Osmium tetraoxide has a tetrahedral structure and, like CF_4, should have four Raman active normal modes of vibration. But ν_1 and ν_3 are within 9 cm^{-1} of each other; and ν_2 and ν_4 are within 10 cm^{-1}. Thus the observed spectrum has two bands — a sharp band at 970 cm^{-1}, and a broad band at 330 cm^{-1}. The 330 cm^{-1} band is split with an approximately 10 cm^{-1} peak separation showing it is the combination of the two bands ν_2 and ν_4. The ν_1 band is apparently much more intense than the ν_3 band, and ν_3 is not observed unless the ν_1 band is suppressed by perpendicularly polarizing the Raman scattered radiation.[331] The effect of temperature on the symmetric stretch (ν_1) and the bending modes ν_2 and ν_4 in OsO_4 is as dramatic as was the effect on the CF_4 vibrational modes. At 398°K in OsO_4 [Figure 22 (p 70)] the ν_1 FWHM bandwidth is approximately 4 cm^{-1} whereas at 1293°K [Figure 26 (p 74)] ν_1 has a definite broadening to the low frequency side reflecting the populating of higher rotational states.

The FWHM bandwidth is approximately 21 cm^{-1}. The FWHM bandwidth of the $\nu_2\nu_4$ band changes only slightly over the same temperature range. The ratio of the peak heights of $\nu_2\nu_4$ to ν_1 range from 0.08 at 398°K to 0.44 at 1293°K showing again that the intensity of the bending modes grows stronger as the temperature increases. The appearance of the broad low shoulder on the high frequency side of $\nu_2\nu_4$ is unexplained, but it is not an artifact of the Raman system.

The increase in intensity and the apparent lack of increase in the bandbreadths of one or both of the bending modes (ν_2 in CF_4, $\nu_2\nu_4$ in OsO_4) with temperature was unexpected. A broadening of the band and a decrease in intensity due to an increase in population of excited rotational and excited vibrational levels was considered the more likely effect for these low energy vibrations. The population in the ground vibrational state is lower at the higher temperatures. Many of the hot band transitions from excited ν_2 (CF_4) and $\nu_2\nu_4$ (OsO_4) vibrational levels to the other vibrational levels would fall in the region of the respective fundamentals, i.e., a transition in CF_4 from ν_2, v = 1 to ν_1, v = 1 would fall at 473 cm^{-1} or near ν_2 and in addition the various harmonics of ν_2 would be near the 435 cm^{-1} fundamental frequency. Thus the increase in intensity in the bending vibrations is due to hot banding. A number of these transitions also fall in the region between the fundamental vibrations (in CF_4, ν_2 v = 1 to ν_3 v = 1 is 825 cm^{-1}, ν_4 v = 1 to ν_3 v = 1 is 629 cm^{-1}, in OsO_4, ν_2 v = 1 to ν_1 v = 1 is 640 cm^{-1}) but except for a weak band at 630 cm^{-1} in OsO_4 no additional bands are observed in the spectra. These hot bands are typically in regions by themselves and may be weak and thus unobserved.

Four possible configurations were considered for the structure of $MReO_4$ (M = K, Rb, Cs, Tl). Those four configurations and their symmetry point groups are depicted below.



If the cation is singly bonded to an oxygen as in structure 1 then of the 12 possible vibrations (3n-6), all are singly degenerate and Raman active. For structure 2 with the cation bridging two oxygens, all 12 possible vibrations are singly degenerate and, again all are Raman active. In structure 3 with the cation bridging three oxygens, the highest probable symmetry is C_{3v} with four doubly degenerate E modes and four singly degenerate A_1 modes. Thus for structure 3 with C_{3v} symmetry, there are eight potentially observable vibrations and all are Raman active. The free ReO_4^- ion has tetrahedral symmetry with four observable vibrational modes, two triply degenerate, one double degenerate, and one singly degenerate. All are Raman active. To summarize, for structures 1-4 the possible number of observable vibrations by Raman spectroscopy are in order 12, 12, 8, and 4.

Reviewing the Raman spectra of the perrhenates [Figures 28 through 36 (pp 76-84)], the remarkable similarity of all the spectra, regardless of the cation, is apparent. In all cases a broad intense band in the regions 300 to 500 cm^{-1} is observed; and in several of the spectra [Figures 32 through 36 (p 80-84)] a weaker band centered around

970 cm^{-1} is present. The 300 to 500 cm^{-1} band appears to be two separate bands in several of the spectra [Figures 28, 33, and 34 (pp 76, 81, and 82)], but the noise level does not allow an unambiguous assignment.

With only two or possibly three bands observed in the Raman spectrum, none of the possible configurations considered can be ruled out. The Raman spectrum of the free ReO_4^- ion in solution shows the two bending modes ν_2 and ν_4 to coincide at 331 cm^{-1}, and the stretching modes ν_1 and ν_3 to be located at 971 cm^{-1} and 918 cm^{-1} respectively.[332] The ν_3 vibration in molecules in the T_d point group typically is weak in the Raman spectrum. Table V (p 101) contains a listing of substituted perrhenates and an osmiamate and their corresponding vibrational frequencies and assignments. The principal interest in these compounds was to observe the magnitude of the shift in the band positions for similar vibrations in the XO_4 and XO_3 (X = Os,Re) portion of the substituted XO_4^-. In the bending vibrations (ν_2 and ν_4 in XO_4, ν_3 and ν_5 in XO_3) the magnitude of the largest shift between the substituted compounds and the free XO_4^- ($\nu_2\nu_4$ = 331 cm^{-1}) is 60 cm^{-1}. The transition assigned to the bending vibrations in our Raman spectra of the perrhenates is very broad (300 to 500 cm^{-1}) and, although a band appears in several of the spectra [Figures 33 and 34 (pp 81 and 82)] in the region of 330 cm^{-1}, generally the location of the center of the peak (or peaks) is uncertain. Thus it is difficult to ascertain whether the peak is shifted from the position of the free ReO_4^- ion or not. The probability for hot banding in this vibration is similar to that discussed in CF_4 and OsO_4. Thus the intensity and bandbreadth of the 300 to 500 cm^{-1} band in the perrhenates may be due almost completely or in part to hot banding and

TABLE V

VIBRATIONAL FREQUENCIES OF AN OSMIAMATE AND SUBSTITUTED PERRHENATES[a]

Compound	Vibrational Frequencies (cm^{-1}) and Assignments					
	ν_1	ν_2 (xo_3)	ν_3	ν_4 (xo_3)	ν_5 oxo	ν_6
ReO_3Cl	435	1001	293	960	344	196
ReO_3Br	195	997	350	963	332	168
ReO_3S^-	504	938	330	891	310	240
K_2ReO_3N	1022	878	315	830	273	380
$NaOsO_3N$	1021	897	309	871	309	312

a. S. O. Ross, "Inorganic Infrared and Raman Spectra," McGraw-Hill, London, 1972, pp. 223-225.

comparison of this band to the bending mode in the free ReO_4^- or the substituted perrhenates is not entirely straightforward. The symmetric stretching vibrations involving ν_2 in the substituted perrhenates experience shifts of 30 cm^{-1} to 100 cm^{-1} from the position of ν_1 (971 cm^{-1}) in the free ReO_4^- ion. The band observed at 970 cm^{-1} in the high temperature Raman spectra of the perrhenates is sharp and is unshifted from the position of the ν_1 transition in the free ReO_4^- ion. When also considered in light of the temperature effect on the bending modes and the symmetric stretching mode set out in the discussion of CF_4 and OsO_4, the vapor phase spectra of the perrhenates would best seem to fit the T_d symmetry configuration. The close resemblance of the spectra to the OsO_4 spectra taken at high temperature also tends to support the T_d structural assignment. The molecular density of the OsO_4 sample was approximately an order of magnitude greater than the molecular density of the perrhenate samples. A spectrum of OsO_4 was run at high temperature and with the laser power level reduced approximately an order of magnitude [Figure 27 (p 75)] from the power level used during the perrhenate spectral runs. This was done to see the effect on the OsO_4 spectrum of a signal to noise ratio similar to that experienced in the perrhenates. The resemblance of this OsO_4 spectrum to the perrhenate spectra again support the conclusion that the 300 to 500 cm^{-1} band in the perrhenates is one or two bands at most, and the ReO_4^- has a tetrahedral symmetry unperturbed by the cation. The spectrum of Cs_2SO_4 [Figure 37 (p 85)] has two bands in the region of the ν_3 and ν_4 modes of the free $SO_4^=$ ion, but it would be very difficult to make a structural assignment for the vapor phase Cs_2SO_4 from this single spectrum.

If the Raman spectra of the perrhenates can best be fit to a molecular structure with tetrahedral symmetry then the location of the cation must be such as not to disturb the symmetry of the anion structure. This can probably best be described by a spherical potential surface about the anion. Wells in the potential surface can now be placed at the four corners of the tetrahedron above the oxygens of the perrhenate, along the lines joining the corners of the tetrahedron and equidistant from the corners, and in the center of each face of the tetrahedron. The depth of the wells are such that they present a low barrier toward escape to large amplitude vibrations. At low temperatures a reasonably rigid structure can be invisioned where the initial cation is located in one of the potential wells. As the temperature is raised, the cation will move into higher vibrational levels until escape becomes possible from the well. Thus as the temperature is raised, the cation can begin to move between potential wells until the energy in the vibrations is such that the cation remains on the spherical potential surface and has no preferred orientation with respect to the anion. Thus the molecule is polytopic or, as this author prefers, dynamorphic. In Table VI (p 104) the vibrational frequencies of a number of matrix isolated ionic ternary compounds are presented. Of particular importance are the vibrations involving the cation, particularly the bending modes. Most all are around 100 cm^{-1} or less, thus population of very high vibrational levels become possible in the temperature ranges considered for vaporization of these molecules. The vibrations involving the metal cation to the perrhenate anion are most probably in this same region. This population of high vibrational levels and the resultant large

TABLE VI

VIBRATIONAL FREQUENCIES AND ASSIGNMENTS OF SOME TYPICAL ARGON MATRIX ISOLATED IONIC TERNARY COMPOUNDS[a]

Compound	Vibrational Frequencies (cm^{-1}) and Assignments					
	ν_1 B=O	ν_2 B-O	ν_3 O-B=O O.P. Bend	ν_4 O-B=O I.P. Bend	ν_5 M-O	ν_6 M-O-B
$LiBO_2$	1976	1094	578	569	471	107
$NaBO_2$	1960	1087	577	573	363	109
KBO_2	1952	1081	581	577	265	88
$RbBO_2$	1951	1080	582	577	225	70
$CsBO_2$	1945	1077	581	576	207	60

	ν_1	ν_2	ν_3	ν_4	ν_5 M-O	ν_6 Cl-O-M	ν_7	ν_8	ν_9 Cl-O-M
$LiClO_3$	966	900	630	557	481	87	1020	533	77
$NAClO_3$	972	914	622	478	305	63	1017	518	52
$KClO_3$	968	922	627	429	256	57	1017	508	46

a. J. P. Devlin in "Advances in Infrared and Raman Spectroscopy," Vol. 2, R. J. H. Clark and R. E. Hester, Eds., Heyden London-New York-Rheine, 1976, p. 153; K. S. Seshadri, L. A. Nimon, and D. White J. Mol. Spectra, 30, 128 (1969).

amplitude of the vibrations is sufficient to allow the cation to escape the potential well and begin to move about on the potential energy surface.

In conclusion the high temperature Raman spectra of the alkali metal and thallium perrhenates have been obtained, and the best fit to the structure has been determined to be a tetrahedral anion whose symmetry is unperturbed by the cation. The molecule has been described as polytopic or "dynamorphic," and a possible description of the mechanism involving cation mobility has been presented.

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LIST OF REFERENCES

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VITA

William Harvey McCulla, son of Phyllis (Honeycutt) Lawrence and the late Samuel Richard McCulla, was born in Birmingham, Alabama, on September 19, 1941. He attended the public schools of Birmingham, Alabama, and was graduated from Woodlawn High School in June 1959. In September 1959, he entered Auburn University and received the Bachelor of Science degree with a major in Chemistry in March 1965. He entered the Graduate School at Auburn University in June 1965, and received the Master of Science degree in August 1968. He entered the Graduate School at The University of Tennessee in September 1975.

He married Bettye L., daughter of Walter and Ouida (Dick) Welsh, in September 1963. He has a son, Allen David, 13 years of age, and a daughter, Kimberly Ann, 11 years of age.