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Citation: The Journal of Chemical Physics **89**, 4666 (1988); doi: 10.1063/1.455686 View online: http://dx.doi.org/10.1063/1.455686 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/89/8?ver=pdfcov Published by the AIP Publishing

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Raman spectra of selected transuranium trihalides in the solid state^{a)}

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(Received 20 May 1988; accepted 12 July 1988)

Raman spectral data have been obtained from a number of transuranium trihalides in the solid state. The Raman spectra of these actinide compounds are reported and compared to the published Raman spectra of isostructural compounds. Tentative symmetry assignments have been made for the observed Raman-active lattice vibrations based on nuclear site symmetry analysis of their respective crystal structures and comparisons to the symmetry assignments made for isostructural lanthanide compounds. The Raman spectral data obtained in this study represent a partial data base for the use of Raman spectroscopy for identifying the crystal structures exhibited by these and isostructural compounds.

INTRODUCTION

Raman spectroscopy has been used to characterize a number of lanthanide sesquioxides, oxyhalides, and trihalides in the solid state.¹⁻⁸ The observed Raman spectra arise from interactions of the laser light with the vibrations of these crystalline ionic compounds. This laser excitation results in quantized vibrations (or motions) of the atoms in the unit cell of the crystal. Since each crystal structure has a unique unit cell, the observed Raman band patterns are, therefore, characteristic of the particular crystal structure exhibited by a specific ionic compound. Such spectra are conveniently referred to as phonon Raman spectra.

The use of Raman spectroscopy to characterize similar actinide compounds has been very limited to date. Prior phonon Raman studies of the actinides have focused primarily on the lighter members (Th through Np).9-12 Bohres et al.⁹ obtained both infrared and Raman spectra of some crystalline actinide tetrachlorides. They calculated valence force constants based on a generalized valence force field for the D_{2d} point group. Goldstein et al.¹⁰ pointed out that the observed vibrational spectra of solid UF₄ and some transition metal tetrafluorides should be interpreted by factor group analysis of the C_{2h}^{6} – $C_{2/c}$ space group rather than the molecular MF₄ group as previously reported.¹¹ The purpose of the present work was to obtain the phonon Raman spectra of selected trivalent transuranium compounds, primarily trihalides, for use in structural studies of these compounds under varying experimental conditions.

The use of phonon Raman spectroscopy as a probe of crystal structure offers some advantages over x-ray diffrac-

J. Chem. Phys. 89 (8), 15 October 1988 4666

0021-9606/88/204666-05\$02.10

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AmF₃, CmF₃, and CfF₃ were prepared by precipitating

with HF the insoluble actinide trifluoride from an aqueous

chloride solution of the trivalent actinide ion. The hydrated

solids were transferred to Ni boats and placed in a Monel

furnace. The solids were first heated to 300 °C in one atmo-

sphere of F₂ gas in order to fluorinate any oxyfluoride impu-

tion techniques in the study of the heavy actinides. For example, the high specific radioactivity of these elements can

cause rapid and extensive damage to the long-range order in

the solid, which degrades the quality of the diffraction pat-

terns that can be obtained. In the case of film techniques, the

emitted radiation can also severely darken the film such that

a useful diffraction pattern is not observed. A Raman spec-

trum can be obtained in a relatively short time and immedi-

ately following an annealing treatment of the sample. In con-

trast, the 3-6 h required to obtain an x-ray diffraction

pattern are often long enough for significant radiation dam-

The isotopes Pu-242, Am-243, and Cm-246/248 which

have been used in this work were synthesized in the high flux

isotope reactor (HFIR) at the Oak Ridge National Labora-

tory (ORNL), as a part of the U.S. Department of Energy's

program for transuranium element production and re-

search. The Cf-249 isotope was obtained isotopically pure

from the beta decay of Bk-249 ($T_{1/2} = 320$ d) which was

also produced at HFIR. These isotopes were processed at the

ORNL Transplutonium Processing Plant (TPP) and puri-

fied using standard solvent extraction and/or ion exchange

age to occur.

techniques.13

Actinide trifluorides

EXPERIMENTAL

Isotopes and purification

a) Research sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy under Grant No. DE-FG05-88ER13865 to the University of Tennessee, Knoxville and Contract No. DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc.

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rity and/or to remove any water. The solids were then heated in vacuum to 600 °C to thermally decompose the tetrafluorides to the trifluorides. The resulting anhydrous trifluorides were loaded into x-ray capillaries which provided primary radiological containment during the characterization studies.

Actinide trichlorides, tribromides, and trilodides

The actinide trihalides $(MX_3: X = Cl, Br, I)$ were prepared using our standard microchemical techniques which have been described previously.¹⁴ The method consists of treating the actinide oxide with anhydrous HX (X = Cl or Br) gas at elevated temperature (~ 500 °C). The hydrohalogenation reactions of the individual actinide oxides were performed in quartz capillaries. In each preparation the samples were melted to ensure purity and completeness of reaction, as evidenced by the observation of a sharp and congruent melting point. In order to prepare the anhydrous triiodides free of oxyiodide impurity, it was necessary to prepare first either the anhydrous trichloride or tribromide. Further treatment of the latter materials with anhydrous HI produced the desired triiodide. Once the desired product was produced, the sample capillary was flame sealed and the sample subjected to characterization studies.

Sample characterization

Raman spectra were obtained with a Ramanor HG-2S spectrophotometer (Jobin Yvon Instruments SA). This spectrophotometer utilizes a double monochromator equipped with curved holographic gratings, a cooled photo-multiplier detector, and pulse counting electronics. A Nico-let 1170 signal averager was used to accumulate spectra from multiple scans. The total scan time required for a reasonable signal-to-noise ratio varied from sample to sample but was in the range of 10–30 min. The 514.5 or 488.0 nm line of an argon-ion laser was used as the excitation source. The Raman scattered light was collected at 90° from the excitation beam. To assure radiological containment of these samples, the sample capillaries were mounted inside a Pyrex test tube. Thus, the Raman spectra were obtained through the layers of quartz and Pyrex.

The actinide samples were also characterized by either solid-state absorption spectrophotometry or x-ray powder diffraction prior to the collection of the Raman data. This was performed to ensure that the samples were exhibiting the expected crystal structure. Where deemed necessary, a subsequent absorption spectral characterization was performed following the Raman experiment to ascertain whether or not a structural change had resulted from the laser excitation/heating.

RESULTS AND DISCUSSION

AmF₃, CmF₃, and CfF₃

These isostructural transplutonium trifluorides exhibited a trigonal crystal structure represented by the space group D_{6h}^3 -P6₃/mcm with six formula units per unit cell.¹⁵ Single crystal polarized Raman studies of isostructural LaF₃,



WAVENUMBER (cm

AmF

FIG. 1. Room-temperature Raman spectra of LaF₃-type trigonal actinide trifluorides. * indicates laser plasma line. ** indicates band due to glass. Excitation wavelength: $AmF_3 = 488.0 nm; CmF_3$ and CfF₃ = 514.5 nm.

PrF₃, and NdF₃, however, led Bauman and Porto¹⁶ to conclude that these compounds exhibited a structure which belongs to the space group $D_{3d}^4 - P\bar{3}c1$. Factor group analysis of this latter structure predicts the following irreducible representation, $\Gamma_{\text{Raman}} = 5A_{1g} + 4E_{1g} + 8E_{2g}$. The room-temperature Raman spectra of these actinide trifluorides are shown in Fig. 1. Although not all of the seventeen Ramanactive bands were observed, these spectra are consistent with room-temperature Raman spectra obtained from isostructural lanthanide trifluorides¹⁶ and are characterized by three bands of strong intensity in the 300-420 cm⁻¹ region. In each spectrum, the Raman-active band of highest frequency occurred as a shoulder. The Raman spectral data from AmF₃, CmF₃, and CfF₃ are compiled in Table I based on the assignments made by Bauman and Porto¹⁶ for the D_{3d}^4 point group.

TABLE I. Raman spectral data (cm⁻¹) from trigonal actinide trifluorides.^a

Mode	AmF ₃	CmF ₃	Cf F ₃
A_18	402	414	420
A_{1g}	(306)	(317)	(321)
A	•••	243	222
A_{1g}	138	106	
E_{1g}	(306)	(317)	(321)
E_{1g}	•••	201	•••
E_{2g}	372	391	394

* Parentheses indicate band which could not be resolved.



FIG. 2. Room-temperature Raman spectra of UCl₃-type hexagonal actinide trichlorides. Excitation wavelength: $AmCl_3 = 488.0 nm; CmCl_3$ and $CfCl_3 = 514.5$ nm.

AmCl_a, CmCl_a, and CfCl_a

The trichlorides of Am and Cm are known to exist only in the UCl₃-type hexagonal structure (space group C_{6h}^2 - $P6_3/m$,^{17,18} while CfCl₃ is dimorphic. It exhibits this hexagonal structure and the PuBr₃-type orthorhombic crystal structure (space group D_{2h}^{17} -Cmcm).¹⁹ Nuclear site symmetry analysis predicts six Raman-active bands for the UCl₃type hexagonal structure, $\Gamma_{\text{Raman}} = 2 A_g + E_{1g} + 3 E_{2g}$, and 12 Raman-active bands for the PuBr₃-type orthorhombic structure, $\Gamma_{\text{Raman}} = 4 A_g + 3 B_{1g} + B_{2g} + 4 B_{3g}$. The Raman spectra obtained from hexagonal AmCl₃, CmCl₃, and CfCl₃ are shown in Fig. 2. Following the symmetry assignments made by Schaack and Koningstein⁴ for singlecrystal hexagonal lanthanide trichlorides, the tentative sym-

TABLE II. Raman spectral data (cm⁻¹) from hexagonal actinide trichlorides.ª

Mode	AmCl ₃	CmCl ₃	CfCl ₃
A	•••	•••	
A _g	(222)	(223)	(233)
E_{1g}	195	196	201
E_{2g}	82	83	76
E_{2g}	188	181	183
E_{2g}	(222)	(223)	(233)

* Parentheses indicate band which could not be resolved.

metry assignments for these actinide trichlorides are given in Table II.

The observed Raman spectrum of orthorhombic CfCl₃ is shown in Figure 3 and the corresponding spectral data are given in Table III. The utility of Raman spectroscopy in differentiating crystal structures can be noted by comparing the spectra of CfCl₃ in both its hexagonal (Fig. 2) and orthorhombic (Fig. 3) modifications. Identification of the crystal structure can be made on the basis of the frequency of the most intense Raman-active band in each spectrum. The intense A_g band for the hexagonal form of CfCl₃ is at 233 cm^{-1} ; whereas, in the orthorhombic form it is at 249 cm⁻¹. Further analysis of the differing band patterns aids in the structural identification.

PuBr₃, AmBr₃, CmBr₃, and CfBr₃

These transuranium tribromides can exhibit either of two crystal structures, the previously mentioned ortho-



FIG. 3. Room-temperature Raman spectra of PuBr₃type orthorhombic CfCl₁ and actinide tribromides. wavelength: Excitation $AmBr_{3} = 488.0$ nm; CfCl₁, PuBr₁, and CmBr₁ = 514.5 nm.



TABLE III. Raman spectral data (cm^{-1}) from orthorhombic actinide trihalides.

Mode	CfCl ₃	PuBr,	AmBr,	CmBr ₃
A	249	154	155	157
A _g	183	113	113	116
Ă,	174	105	108	110
A _g	51	43	43	44
B _{1g}	199	130	131	133
B _{2g}	117		•••	
B _{3g}	83	79	80	82

rhombic structure and the AlCl₃-type monoclinic structure. PuBr₃ is the prototype compound for the orthorhombic structure, space group D_{2h}^{17} -Cmcm.²⁰ AmBr₃ and CmBr₃ are also known to crystallize in this structure.¹⁷ CfBr₃ has been reported to exhibit the PuBr₃-type orthorhombic structure following the application of pressure to its monoclinic form²¹ and as the result of the beta decay of orthorhombic ²⁴⁹BkBr₃.²² As mentioned above, 12 Raman-active bands are expected for this orthorhombic structure. The Raman spectra of these orthorhombic actinide tribromides are shown in Fig. 3. The spectrum of each of these orthorhombic tribromides (Pu, Am, and Cm) is comparable to the Raman spectra obtained from isostructural NdBr₃ and SmBr₃.²³ They are also in agreement with the Raman spectrum of isostructural, orthorhombic CfCl₃. Based on our earlier symmetry assignments²³ for NdBr₃, the Raman spectral data from these orthorhombic trihalides are given in Table III.

The utility of phonon Raman spectroscopy as a probe of crystal structure is further demonstrated if comparisons are made between the Raman spectra of orthorhombic $CfCl_3$ and orthorhombic $PuBr_3$. Although the vibrational energies are shifted to lower frequency in the tribromide spectra compared to those in the spectrum of $CfCl_3$, the overall Raman band patterns are very similar. Because of the complicated motions of these normal modes, the observed frequencies cannot be directly correlated with any physical property, i.e., formula mass, formula volume, density, etc. Thus, the Raman band pattern appears to be independent of the metal ion and only frequency shifted with a change in the halide ion.

CfBr₃ is known to exist in two crystal forms. The AlCl₃type monoclinic form (space group $C_{2h}^3 - C2/m$)²⁴ is produced by the hydrobromination reaction on CfO_{2-x}. An orthorhombic (PuBr₃-type) form is also known and is only produced by the beta decay of orthorhombic ²⁴⁹BkBr₃²² or by the application of pressure to the monoclinic form of CfBr₃.²¹ Nuclear site symmetry analysis of the monoclinic structure predicts 12 Raman-active bands, $\Gamma_{Raman} = 6 A_g$ + $6B_g$. However, only six bands are observed in the Raman spectrum of monoclinic CfBr₃. The reason for only six observed bands relates to the details of the structure of the compound. It consists of layered "sandwiches." The "sandwich" consists of a layer of metal ions in a hexagonal arrangement sandwiched between two layers of halogen ions. These individual sandwiches are then stacked to make the full three-dimensional structure. If there are no intersandwich interactions, the observed lattice vibrations result from motions in the individual sandwiches. Factor group analysis of an individual sandwich, which possesses D_{3d}^1 symmetry, predicts only six Raman-active bands, $\Gamma_{\text{Raman}} = 2A_{1g} + 4E_g$. The observed room-temperature Raman spectrum of CfBr₃ is shown in Fig. 4. The corresponding Raman spectral data are compiled in Table IV.

Attempts were made to obtain the Raman spectrum of the orthorhombic form of CfBr₃. These experiments were performed on aged samples of the orthorhombic form of ²⁴⁹BkBr₃. The solid-state absorption spectrum of a ten-yearold sample of ²⁴⁹BkBr₃ was obtained prior to the Raman experiment to ensure that the sample was exhibiting the



FIG. 4. Room-temperature Raman spectra of AlCl₃-type monoclinic CfBr₃ and BiI₃type rhombohedral actinide triiodides. * indicates band due to molecular I₂. Excitation wavelength: AmI₃ = 488.0 nm; CfBr₃, CmI₃, and CfI₃ = 514.5 nm.

TABLE IV. Raman spectral data (cm⁻¹) from monoclinic and rhombohedral actinide trihalides.

Mode	CfBr ₃	AmI ₃	CmI ₃	CfI ₃
A 10	159	117	119	118
A_{1g} E_{g}	60	49	49	50
	171	125	130	130
E_{s}	126	90	94	93
E,	76	58	61	60
Ê,	42	33	35	34

orthorhombic structure. The absorption spectra of both the monoclinic and orthorhombic forms of CfBr₃ have been previously described²² and provide an easy and efficient structural identification. The sample of ²⁴⁹BkBr₃, which contained approximately 0.04% BkBr3 and 99.96% CfBr3, was examined using an argon-ion laser (514.5 nm). The power level was set at 30 mW in order to minimize laser heating. A Raman spectrum was not obtained from this sample and subsequent analysis by absorption spectrophotometry revealed that the sample had converted to the monoclinic form. The inability to obtain a Raman spectrum from either form of this aged sample is unexplained but is likely due to poor crystallinity. This may be the result of ten years of β radiation from the Bk parent and α radiation from the ingrowing Cf daughter which would cause significant radiation damage to the sample's long-range order. The shortrange order in the sample remained intact, however, and it is this which is sampled by solid-state absorption spectrophotometry. The laser heating that occurred and produced the structural transformation did not cause sufficient annealing of the sample to restore the long-range order needed to effect the characteristic vibrations of the crystal lattice.

Ami₃, Cmi₃, and Cfi₃

The three transplutonium triiodides are isostructural^{17,25} and exhibit the BiI₃-type rhombohedral structure, space group $C_{3i}^2 - R \overline{3}$. Nuclear site symmetry analysis of this structure predicts eight Raman-active bands, $\Gamma_{\text{Raman}} = 4A_g$ $+4 E_{o}$. This rhombohedral structure is identical to the AlCl₃-type monoclinic structure except for the packing of the halogen layers of the sandwiches. In the rhombohedral structure, the halogen layers are packed in a hexagonal closest-packed arrangement, whereas in the monoclinic structure the halogen layers are packed in a face-centered cubic arrangement. The individual sandwiches, however, are the same, and thus the observed Raman spectra are the same. The irreducible representation for the normal modes of the rhombohedral sandwich is the same as previously stated for the monoclinic sandwich, $\Gamma_{\text{Raman}} = 2A_{1g} + 4E_g$. In Fig. 4 are shown the Raman spectra of these rhombohedral actinide triiodides. The observed band frequencies are different but the characteristic band pattern is the same as that seen in the Raman spectrum of monoclinic CfBr₃ (Fig. 4, top). The Raman spectral data from AmI_3 , CmI_3 , and CfI_3 are compiled in Table IV.

CONCLUSIONS

The room-temperature phonon Raman spectra of a number of crystalline actinide compounds have been obtained. Tentative symmetry assignments have been made, where possible, for the observed Raman-active bands by analogy to assignments made for isostructural compounds. Since these Raman bands result from motions of the atoms in the lattice of these ionic crystals, many crystal structure changes can be monitored by Raman spectroscopy. These Raman spectra will serve as a partial data base for further investigations of the structural relationships exhibited by these compounds under varying experimental conditions.

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