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COVALENCY OF NEPTUNIUM(IV) ORGANOMETALLICS FROM  $^{237}\text{Np}$   
MÖSSBAUER SPECTRA

by

D. G. Karraker

E. I. du Pont de Nemours & Co.  
Savannah River Laboratory  
Aiken, SC 29808

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ABSTRACT

The isomer shifts in  $^{237}\text{Np}$  Mössbauer spectra arise from the shielding of neptunium's 6s orbitals by the inner 5f orbitals. In covalent bonding, ligand contributions to the 5f electron density increase the shielding, and the  $^{237}\text{Np}$  isomer shift reflects differences in bond character among covalently bonded ligands. The large difference in isomer shift (3.8 cm/sec) between ionic Np(IV) and Np(III) compounds permits a good determination of ligand bonding differences in Np(IV) organometallic compounds. The Mössbauer spectra for about 20 Np(IV) organometallic compounds, principally cyclopentadienyl (Cp) compounds of the general composition  $\text{Cp}_x\text{NpX}_{4-x}$  ( $x = 1, 2, 3$ ;  $X = \text{Cl}, \text{BH}_4, {}^n\text{Bu}, \text{Ph}, \text{OR}, \text{acac}$ ), show both the differences in  $\sigma$  bonding among the X ligands, as well as the covalent effect of the Cp ligands.

## I. INTRODUCTION

The  $^{237}\text{Np}$  Mössbauer Effect (ME) has been especially valuable for chemical and physical studies of solid neptunium compounds. The isomer shift in  $^{237}\text{Np}$  has a very wide range – from -6.9 cm/sec to +3.5 cm/sec, and excellent resolution can be obtained without excessively elaborate equipment. Neptunium forms compounds in five valence states, plus the metallic state, so a wide range of compounds and intermetallic materials can be prepared for Mössbauer studies. Examples of some past Mössbauer studies are magnetic properties of some neptunium compounds(2-5) and localization of 5f electrons in Np intermetallics(6). This paper outlines the theory and experimental procedure for  $^{237}\text{Np}$  Mössbauer studies and presents the application of the  $^{237}\text{Np}$  ME to the determination of covalent effects in Np organometallic compounds.

## $^{237}\text{Np}$ MÖSSBAUER EFFECT

### A. Description

Stone and Pillinger(7) discovered the ME of  $^{237}\text{Np}$  at the Savannah River Laboratory, and the experimental techniques were further developed by the group at Argonne National Laboratory, then directed by G. M. Kalvius. The physics of the  $^{237}\text{Np}$  has been summarized in three excellent reviews(8,9,10) and will be discussed only briefly here.

The gamma ray used in the  $^{237}\text{Np}$  ME results from the 59.5 keV,  $5/2^- \rightarrow 5.2^+$  E1 transition in  $^{237}\text{Np}$  ( $t_{1/2}$ , 63 nsec). The 59.5 keV level is accessible from the  $\alpha$ -decay of  $^{241}\text{Am}$ ,  $\beta$ -decay from  $^{237}\text{U}$ , or electron-capture decay from  $^{237}\text{Pu}$ . The half-life of  $^{241}\text{Am}$  (433 years) makes it the obvious choice for a Mössbauer source.

## B. Hyperfine Interactions

Hyperfine interactions refer to the interaction of the  $^{237}\text{Np}$  nucleus with the surrounding electromagnetic field (internal or external). The interpretation of  $^{237}\text{Np}$  Mössbauer spectra depends upon the analysis of hyperfine effects. The Hamiltonian for the ME system has three terms:

$H_{\text{hf}} = H_{\text{IS}} \pm H_{\text{Q}} \pm H_{\text{M}}$ , where  $H_{\text{IS}}$  refers to interactions of the central field with the nucleus;  $H_{\text{Q}}$  represents the interaction between the quadrupole moment with the electric field gradient; and  $H_{\text{M}}$  is the interaction of magnetic fields with the nucleus. The splitting of the excited and ground states by hyperfine fields is illustrated in Figure 1 for single unsplit levels, quadrupole-split levels, magnetically split levels and combined magnetic and quadrupole split levels(11).

## C. Isomer Shift

The central field interaction is the result of the Coulomb interaction of the electronic charge with the nuclear charge. This interaction determines the isomer shift. The central field

interactions, which lead to the isomer shift in ME, are spherically symmetric and depend principally upon S orbitals. For  $^{237}\text{Np}$  ME, 6s orbitals are shielded from the nucleus by the inner 5f orbitals (Figure 2). Increases in the electron density in the 5f orbitals increase the shielding of the 6s orbital and produce a more positive isomer shift. 6d and 6p electrons can also shield the 6s orbitals, but their contributions are small compared to the effect of 5f shielding. An obvious example of the effect of 5f electron density on the isomer shift is the differences in the isomer shift for neptunium compounds of different valences, which amount to 2-4 cm/sec between consecutive valences, and a range over 10 cm/sec between  $\text{Np}^{7+}$  and  $\text{Np}^{3+}$  (Figure 3).

Given these large differences in isomer shifts between valences, covalent effects on bonding can also be identified by isomer shifts (12). Covalency requires the overlap of ligand orbitals with the 5f orbitals, which increases the 5f electron density with a consequent positive increase in the isomer shift. The comparison of isomer shifts between neptunium fluorides and oxygen-bonded neptunium compounds (Figure 3) shows the strong shift toward lower valence of the  $\text{NpO}_2^{++}$  and  $\text{NpO}_2^+$  compounds compared to that of  $\text{NpF}_6$  and  $\text{NpF}_5$ . The electron density contributed to the 5f orbitals of the  $\text{Np}^{6+}$  and  $\text{Np}^{5+}$  ions by the tightly bonded oxygen ligands results in an isomer shift toward lower valence. For the  $\text{Np}^{4+}$ , the contribution of oxygen ligands

is small, because it becomes more difficult for the orbitals to overlap in the larger  $\text{Np}^{4+}$  ion. In the still larger  $\text{Np}^{3+}$  ion, essentially no difference in the isomer shifts occurs between a fluoride and an oxygen ligand environment.

#### D. Quadrupole Interaction

The interaction of the nuclear quadrupole tensor and the electric field gradient tensor from the ionic environment surrounding the Np ion can result in Stark (electric field) splitting of the nuclear levels, or quadrupole splitting. In general, quadrupole splitting requires the alignment of the z-component of the electric field gradient of the unfilled 5f electron shell(9). This alignment must be produced by an external field, because, otherwise, rapid rotation of the electric field gradient allows only an average to be observed.

Quadrupole interactions can be reduced to combinations of two components — the electric field gradient and the asymmetry parameter,  $\eta$  (13). For an Np ion in a site with an n-fold rotation or rotation-reflection axis with  $n > 2$ , the asymmetry parameter  $\eta = 0$ , and the resonance is split into five equally spaced lines. At the other extreme, where  $\eta = 1$ , the resonance is split into three lines. Intermediate values of  $\eta$  are represented by unequal, five-line spectra. In all cases, the central resonance of the quadrupole spectrum has the same isomer shift as the unsplit resonance would have (Figure 1).

## E. Magnetic Interaction

The interaction of the nuclear energy levels with a magnetic field (internal or external) results in magnetic splitting of the  $^{237}\text{Np}$  Mössbauer spectra (Figure 1). Normally, a paramagnetic ion will have a magnetic field at the nucleus because of its unpaired electrons. At room temperature, the direction of the field changes too rapidly for the nucleus to respond. At low temperatures, the relaxation time is greatly decreased, often to the point where the  $^{237}\text{Np}$  Mössbauer spectrum is magnetically split. When the absorbing compound becomes ferromagnetic or antiferromagnetic, the relaxation time becomes infinite on the  $^{237}\text{Np}$  Mössbauer time scale, and a large magnetic splitting normally results. Pure magnetic splitting has a 16-line pattern (Figure 1), but as the energies of some of the resonances are nearly the same, the spectrum usually shows only eight to ten lines. The average of two symmetrically split lines determines the isomer shift in magnetically split spectra. Occasionally, quadrupole splitting may be also imposed on magnetic splitting, but since the magnetic splitting is normally much greater than quadrupole splitting, no serious complication is introduced in interpreting the spectrum. Where quadrupole and magnetic splitting are nearly equal, as for some  $\text{NpO}_2^{++}$  or  $\text{NpO}_2^+$  compounds, assignment of the resonances becomes very difficult.



## F. Intermediate Relaxation Effects

The discussion of hyperfine interactions involves the assumption that the hyperfine fields are time independent. For some compounds, time-dependent effects (intermediate relaxation) influence the Mössbauer spectrum.

The electrons in the unfilled shell of the neptunium ion can be considered to alternate between "spin-up" and "spin-down" positions under the influence of external fields on the ion. The electronic relaxation time is the period required for the spin flip. If the relaxation time is slow, compared to the Larmor precession frequency of the nucleus and the lifetime of the excited state, the nucleus will see a static field, and the spectrum will be magnetically split. Fast relaxation times average the field on the nucleus to zero, and single-line or quadrupole spectra will result. Intermediate relaxation times are of the same order as the Larmor precession frequency and the excited-state lifetime, and result in a loss of resolution of the Mössbauer spectrum, often so much so that the spectrum becomes an uninterpretable smear (Figures 4,5). Relaxation is considered to occur principally through spin-lattice and spin-spin interactions, although other mechanisms have been considered(14). Physical methods of avoiding intermediate relaxation effects depend upon changing the experimental conditions to favor faster (higher temperatures) or slower (external magnetic fields, lower temperatures) relaxation times. In practice, such methods are

not easy to apply and not necessarily successful. However, in some cases, intermediate relaxation effects can be avoided by changing the chemical compound to a similar compound that retains the features under study. Substitution of a bulkier ligand or cation [MeCp for Cp,  $N(C_2H_5)_4^+$  for  $Cs^+$ ] often reduces relaxation effects without affecting the object of the study. Bulkier ligands increase the distance between Np ions, thus reducing the spin-spin interactions that affect relaxation.

#### *Experimental Techniques*

The experimental apparatus and techniques for  $^{237}\text{Np}$  Mössbauer spectroscopy have been included in earlier reviews(8,9,15,16,17). The instrumentation used in Mössbauer studies has always been similar among different workers, but there were some differences in sources, detectors, standardization of spectra, etc., particularly before the year 1972. In recent years, some techniques have become standard; they will be emphasized in the section on "Instrumentation."

#### *Instrumentation*

$^{237}\text{Np}$  Mössbauer experiments have usually used a conventional constant-acceleration spectrometer in transmission geometry(18). The spectrometer must achieve relatively high velocities ( $\pm 20$  cm/sec) while operating at liquid helium temperatures. The recoilless fraction for  $^{237}\text{Np}$  ME is severely decreased above helium temperatures for most absorbers, so the source-absorber equipment requires a

liquid helium dewar, preferably one capable of maintaining helium temperatures for three to four days. A convenient velocity calibration can be obtained from a  $\text{NpAl}_2$  absorber, which has a well-characterized magnetically split spectrum at 4.2 K.

### *Sources*

The most convenient source is  $^{241}\text{Am}$  metal as a 5% alloy in cubic thorium metal matrix. A 433-year  $^{241}\text{Am}$  source lasts indefinitely; one such source has been used satisfactorily at the Savannah River Laboratory (SRL) for about ten years. About three mg  $^{241}\text{Am}$  in a source yields counting rates above  $10^4$  counts/channel-min. Sources in earlier work used  $^{237}\text{U}$  (6.75 d), and the use of  $^{237}\text{Pu}$  (44.6 d) has been considered, but the half-lives of both isotopes are quite inconvenient; the  $^{241}\text{Am-Th}$  source has the narrowest experimental line width yet achieved, about 0.1-0.2 cm/sec(15).

### *Standards*

The single line spectrum of  $\text{NpAl}_2$  at 77 K is the recommended zero of isomer shift (19). This zero can be determined with more precision than a zero based upon the single resonance line of  $\text{NpO}_2$ . The  $\text{NpO}_2$  resonance is broadened by a weak magnetic splitting below 25 K, and is thus much less satisfactory, though often used in early work. In practice, the centroid of the  $\text{NpAl}_2$  spectrum at 4.2 K is normally used as zero isomer shift. As noted before, the magnetically split spectra of  $\text{NpAl}_2$  can simultaneously provide a convenient velocity calibration.

### *Detectors*

Two detectors are in use — NaI(Tl) scintillation crystals and Ge(Li) semiconductors. Both are satisfactory. The detector in current use at SRL is a NaI(Tl) scintillation counter. This counter has been quite satisfactory over several years of service and avoids the liquid-nitrogen cooling necessary for Ge(Li) detectors. The window of the single-channel analyzer is adjusted to accept the 59.54 keV photopeak for all three detectors.

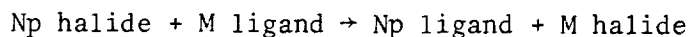
### *Absorbers*

$^{237}\text{Np}$  can be obtained in gram quantities for preparation of absorbers for study. The specific activity of  $^{237}\text{Np}$  is  $1.57 \times 10^6$   $\alpha$ /min-mg, and quantities greater than a few mg should be handled in a glove box or other form of containment to prevent contamination of the laboratory with alpha activity. Most Np organometallic compounds are decomposed by water and oxygen (often violently!), so preparation of the compounds, preparation of the absorbers, etc., is performed in an inert atmosphere glove box. The absorbers are usually prepared by 1) packing the powdered sample in a plastic holder, 2) covering the powder with a plastic plug, and 3) wrapping the assembly with adhesive polyester tape. The absorber is removed from the glove box and wrapped with an additional layer of plastic tape to prevent the spread of alpha activity. Normally, about 50 mg  $\text{Np}/\text{cm}^2$  is adequate for most materials. Crystalline solids, such as  $\text{NpCl}_4$ ,  $\text{NpBr}_4$ ,  $\text{NpCl}_3$ , etc., have larger recoilless fractions than the

essentially amorphous Np organometallic compounds, which can require three to four days to develop an acceptable spectrum.

### *Compounds*

The Np organometallic compounds used in this study were prepared (most for the first time) by using the general procedures developed in the synthesis of the analogous uranium compounds. Some modification of the procedures was necessary, since  $\text{Np}^{4+}$  is more easily reduced than  $\text{U}^{4+}$ . The basic reaction used in nearly all preparations is



M = alkali or Tl

In general, metallated ligands are strong reducing agents, so often a  $\text{Np}^{3+}$  organometallic is the major product, rather than the desired  $\text{Np}^{4+}$  organometallic. Adjustment of experimental conditions was occasionally successful in obtaining the desired  $\text{Np}^{4+}$  product.

## II. $^{237}\text{Np}$ ISOMER SHIFT AND COVALENCY

### A. $\text{NpCp}_3\text{X}$ Compounds

The first actinide organometallic compound prepared was tris(cyclopentadienyl) uranium(IV) chloride,  $\text{U}(\text{C}_5\text{H}_5)_3\text{Cl}$  (hereafter,  $\text{C}_5\text{H}_5^-$  is abbreviated "Cp") (20), and its preparation was succeeded by the preparation of Cp compounds of the +3 and +4-valent actinide ions up to  $\text{Cf}^{3+}$  (21). With few exceptions, the organometallic compounds of the actinides include the Cp ligand in their structure; by reacting  $\text{UCp}_3\text{Cl}$  (or  $\text{NpCp}_3\text{Cl}$ ) with an alkali metal

ligand compound, such as  $\text{Li}^n\text{Bu}$ ,  $\text{LiPh}$ ,  $\text{NaO}^n\text{Bu}$ , etc., the ligand replaces the chloride ion, forming  $\text{NpCp}_3^n\text{Bu}$ ,  $\text{NpCp}_3\text{Ph}$ ,  $\text{NpCp}_3\text{O}^n\text{Bu}$ , etc. Quite a variety of compounds have been prepared in this manner from  $\text{UCp}_3\text{Cl}$ , most of which can also be prepared from  $\text{NpCp}_3\text{Cl}$ . Substituted Cp ligands, such as  $\text{CH}_3\text{-C}_5\text{H}_4^-$  (MeCp), form analogous compounds.

The isomer shifts in  $^{237}\text{Np}$  Mössbauer spectra of these compounds are normally displaced from an ionic  $\text{Np}^{4+}$  isomer shift toward the  $\text{Np}^{3+}$  isomer shift. Using the variety of compounds that can be prepared as derivatives of the  $\text{NpCp}_3^+$  moiety and selecting appropriate standards, a comparison of the bonding properties of the ligands can be obtained from their  $^{237}\text{Np}$  Mössbauer spectra. Compounds containing one or two Cp ligands per  $\text{Np}^{4+}$  ion have also been prepared. These compounds afford a measure of the effect on the  $^{237}\text{Np}$  isomer shift of adding one, two, or three Cp ligands.

Unfortunately, the  $^{237}\text{Np}$  Mössbauer spectra of  $\text{NpCp}_3\text{X}$  compounds are strongly affected by intermediate relaxation effects. Attempts to counter relaxation effects by synthesizing compounds that substitute MeCp for Cp or  $\text{C}_6\text{H}_4\text{C}_2\text{H}_5$  for  $-\text{C}_6\text{H}_5$ , etc., often succeeded in obtaining interpretable, although not necessarily ideal, spectra. Figure 6 shows the spectra of  $\text{NpCp}_3\text{BH}_4$  and  $\text{Np}(\text{MeCp})_3\text{BH}_4$ , illustrating a successful example where an isomer shift could be obtained from the spectrum of the substituted compound but not from the parent compound. Analysis of the results in terms of the ligand's

properties involves the assumption that the effect of substituted ligands and unsubstituted ligands on the isomer shifts is the same; data given later in this paper support this assumption. The  $^{237}\text{Np}$  Mössbauer spectrum of  $\text{NpCp}_3\text{OCH}(\text{CH}_3)_2$  is shown in Figure 7, and spectra for  $\text{Np}(\text{acac})_2\text{Cl}_2 \cdot \text{THF}$  ("acac" =  $\text{CH}_3\text{COCHCOCH}_3$ ) and  $\text{Np}(\text{acac})_2(\text{MeCp})_2$  are shown in Figures 8 and 9, respectively. The latter two spectra allow a comparative isomer shift for  $\text{Cp}_2\text{NpX}_2$  compounds to be derived. Mössbauer parameters for  $\text{Np Cp}_n\text{X}_{4-n}$  compounds are shown in Table I.

To compare the contributions of the ligands, the assumption is made that  $\text{Cl}^-$  and  $\text{BH}_4^-$  ions make no covalent contributions, and  $\text{NpCp}_3\text{Cl}$  or  $\text{Np}(\text{MeCp})_3\text{BH}_4$  and  $\text{NpCl}_4$  can be used as reference compounds. To determine the effect of two Cp ligands,  $\text{Np}(\text{acac})_2\text{Cl}_2 \cdot \text{THF}$  was used as a reference, since the acac ligands made a strong negative change in the normal  $\text{Np}^{4+}$  isomer shift. The isomer shifts assigned to each ligand are shown in Table II.

The isomer shift differences in Table II show that only Cp ligands make a positive covalent contribution. Moreover, the  $\text{Cp}_3\text{Np}^+$  moiety is unusually stable;  $\text{Cp}_2\text{Np}^{2+}$  shows about half the isomer shift difference of the  $\text{Cp}_3\text{Np}^+$  unit, and the effect of a single Cp ligand is so slight that Cp in  $\text{NpCpCl}_3$  is probably  $\sigma$ -bonded. The isomer shift differences show clearly that alkyl, aryl, and alkoxide ligands are  $\sigma$ -bonding. The alkyl and aryl ligands are very strongly  $\sigma$ -bonding, equivalent to about 25% of the difference in the  $\text{Np}^{3+}$  -  $\text{Np}^{4+}$  isomer shifts. The isomer shift differences of the alkoxide ligands average 0.55 cm/sec, about

half the alkyl-aryl shift difference, and are consistent with the greater stability of the Np-OR bond. The precision of the data does not allow a distinction between the isomer shifts of the alkyl and aryl ligands, or among the alkoxide ligands. The chemical stability of NpCp<sub>3</sub>Ph and NpCp<sub>3</sub>Ar compounds depends upon the covalent contribution of the three-Cp ligands offsetting the strong electron-withdrawing nature of the Np-R and Np-Ar bonds.

#### B. Bond Length and Isomer Shift

The <sup>237</sup>Np Mössbauer isomer shifts (Table III) of NpCp<sub>4</sub>- and Np(COT)<sub>2</sub>-type compounds (COT = C<sub>8</sub>H<sub>8</sub><sup>-2</sup>, the cyclooctatetraenyl dianion) show anomalously small isomer shifts for the NpCp<sub>4</sub> compounds, when compared to Np(COT)<sub>2</sub> or NpCp<sub>3</sub>Cl ( $\delta$  = 1.4). The substitution of a fourth Cp ligand into NpCp<sub>3</sub>Cl would not be expected to decrease the isomer shift to 0.72 cm/sec (NpCp<sub>4</sub>). The COT and Cp ligands are 10- and 5-electron donors, respectively, so NpCp<sub>4</sub> and Np(COT)<sub>2</sub> both have the same electron density available for bonding.

An explanation for this apparent anomaly is found by considering the metal-carbon bond lengths of the uranium analogues of these compounds. The average uranium-ring carbon distances have been determined crystallographically to be 2.65 Å for U(COT)<sub>2</sub>, 2.74 Å for (UCp<sub>3</sub>Cl), and 2.81 Å for UCp<sub>4</sub> (27). The bond distances for the isostructural Np-COT and Np-Cp compounds should be slightly, but not significantly smaller. The addition of a fourth Cp ligand to the UCp<sub>3</sub><sup>+</sup> moiety creates sufficient



ligand repulsion that the uranium-ring carbon distance of  $\text{UCp}_4$  is  $0.07 \text{ \AA}$  greater than that of  $\text{UCp}_3\text{Cl}$ , and  $0.16 \text{ \AA}$  longer than that of  $\text{U}(\text{COT})_2$ . As applied to the covalency of the neptunium compounds, the longer-bond distance decreases the overlap of the neptunium 5f and the ligand orbitals and is reflected in a smaller covalent isomer shift.

A second example of the effect of bond distance is found by comparing the isomer shift range of  $\text{Np}^{3+}$  organometallics (Table IV) with the isomer shift range of  $\text{Np}^{4+}$  organometallics. The extreme range of isomer shifts for  $\text{Np}^{3+}$  organometallics is about  $0.4 \text{ cm/sec}$ , while  $\text{Np}^{4+}$  organometallics have isomer shifts covering a range of about  $2.5 \text{ cm/sec}$ . The probable explanation lies in the sizes of the neptunium ions —  $\text{Np}^{4+}$  has an ionic radius of  $0.98 \text{ \AA}$ ;  $\text{Np}^{3+}$  an ionic radius of  $1.04 \text{ \AA}$  (28). The 5f orbitals of the  $\text{Np}^{3+}$  ion are spatially less accessible than those of  $\text{Np}^{4+}$ , and the smaller interaction between the 5f and ligand orbitals is reflected in small isomer shift effects.

The results of  $^{237}\text{Np}$  Mössbauer spectra provide a picture of the bonding of  $^{237}\text{Np}$  organometallics and their uranium analogues that could be obtained by no other method. In essence, Mössbauer results give a view of the compound from the position of the neptunium nucleus; the work summarized in this paper shows that the  $^{237}\text{Np}$  isomer shift results are consistent with available data and provide a useful picture of the bonding in actinide organometallics.

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TABLE I

Mössbauer Parameters for  $\text{Np-Cp}_n\text{-X}_{4-n}$  Compounds

Compound	Isomer Shift, <sup>(a)</sup> $\delta$ , cm/sec	Quadrupole Coupling Constant $eqQ/4$ , cm/sec	Magnetic Hyperfine Constant $g_0^{\text{N}} H_{\text{eff}}$ , cm/sec	Reference
$\text{NpCp}_3\text{Cl}$	$1.4 \pm 1.0$			22
$\text{Np}(\text{MeCp})_3\text{BH}_4$	$1.45 \pm 0.4$			23
$\text{NpCp}_3^{\text{nBu}}$	$0.27 \pm 0.07$		$5.8 \pm 0.2$	23
$\text{NpCp}_3\text{C}_6\text{H}_4\text{C}_2\text{H}_5$	$0.42 \pm 0.28$		$5.5 \pm 0.4$	23
$\text{Np}(\text{MeCp})_3\text{O}^i\text{Pr}$	$0.93 \pm 0.07$	$5.0 \pm 1.0$	$5.7 \pm 0.2$	23
$\text{NpCp}_3\text{O}^i\text{Pr}$	$0.86 \pm 0.2$		$5.4 \pm 0.5$	23
$\text{NpCp}_3\text{OCH}(\text{CF}_3)_2$	$0.79 \pm 0.3$		$5.7 \pm 0.5$	23
$\text{NpCp}_3^t\text{Bu}$	$0.86 \pm 0.3$		$5.2 \pm 0.06$	23
$\text{Np}(\text{MeCp})\text{Cl}_3 \cdot 2\text{THF}$	$-0.31 \pm 0.07$		$5.15 \pm 0.06$	23
$\text{Np}(\text{acac})_2\text{Cl}_2 \cdot \text{THF}^{(b)}$	$-1.47 \pm 0.07$	$0.97 \pm 0.15$	$7.92 \pm 0.15$	} this work
$\text{Np}(\text{MeCp})_2(\text{acac})_2$	$-0.53 \pm 0.07$			
$\text{NpCl}_4^{(b)}$	$-0.35 \pm 0.05$	$-0.42 \pm 0.05$	$4.74 \pm 0.05$	13
$\text{NpCl}_3^{(b)}$	$3.54 \pm 0.05$	$0.49 \pm 0.05$		8

<sup>(a)</sup> referred to  $\text{NpAl}_2 = 0$ <sup>(b)</sup> included for comparison

TABLE II

 $^{237}\text{Np}$  Isomer Shifts for Ligands

<i>Bond</i>	<i>Compound</i>	$\delta$ , <i>cm/sec</i>	<i>Reference</i>	$\Delta\delta$
$\text{Cp-NpX}_3$	$\text{Np}(\text{MeCp})\text{Cl}_3 \cdot 2\text{THF}$	-0.31	$\text{NpCl}_4$	+0.04
$\text{Cp}_2\text{-NpX}_2$	$\text{Np}(\text{acac})_2(\text{MeCp})_2$	-0.53	$\text{Np}(\text{acac})_2\text{Cl}_2 \cdot \text{THF}$	+0.94
$\text{Cp}_3\text{-NpX}$	$\text{NpCp}_3\text{Cl}$	1.4	$\text{NpCl}_4$	+1.75
	$\text{Np}(\text{MeCp})_3\text{BH}_4$	1.45	$\text{NpCl}_4$	+1.80
$\text{R-NpCp}_3$	$\text{NpCp}_3^{\text{nBu}}$	0.27	$\text{NpCp}_3\text{Cl}$	-1.13
$\text{Ar-NpCp}_3$	$\text{NpCp}_3\text{C}_6\text{H}_4\text{C}_2\text{H}_5$	$0.42 \pm 0.5$	$\text{NpCp}_3\text{Cl}$	-0.98
$\text{RO-NpCp}_3$	$\text{Np}(\text{MeCp})_3\text{O}^i\text{Pr}$	0.93	$\text{NpCp}_3\text{Cl}$	-0.47
	$\text{NpCp}_3\text{O}^i\text{Pr}$	0.86	$\text{NpCp}_3\text{Cl}$	-0.56
	$\text{NpCp}_3\text{OCH}(\text{CF}_3)_2$	0.79	$\text{NpCp}_3\text{Cl}$	-0.61
	$\text{NpCp}_3\text{O}^t\text{Bu}$	0.86	$\text{NpCp}_3\text{Cl}$	-0.56
$(\text{acac})_2\text{-NpCl}_2$		-1.47	$\text{NpCl}_4$	-1.13

TABLE III

Isomer Shifts of  $\text{NpCp}_4$  and  $\text{Np}(\text{COT})_2$  Compounds

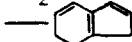
Compound	Isomer Shift, $\text{cm/sec}^a$	Magnetic Coupling Constant $g_0^{14}\text{N} \text{ } H_{\text{eff}}$ , $\text{cm/sec}$	Quadrupole Coupling Constant $eqQ/4$ , $\text{cm/sec}$	Reference
$\text{NpCp}_4$	$0.72 \pm 0.02$	-	$1.66 \pm 0.02$	22
$\text{Np}(\text{MeCp})_4$	$0.71 \pm 0.7$	-	$1.29 \pm 0.08$	25
$\text{Np}(\text{COT})_2$	$1.94 \pm 0.05$	$6.12 \pm 0.05$	$-0.46 \pm .05$	24
$\text{Np}(\text{EtCOT})_2$	$1.90 \pm 0.10$	$6.15 \pm 0.10$	$-0.5 \pm 0.02$	25
$\text{Np}(\text{BuCOT})_2$	$1.94 \pm 0.05$	$6.10 \pm 0.05$	$0.46 \pm 0.05$	25

<sup>a</sup>. Referred to  $\text{NpAl}_2 = 0$ 

TABLE IV

Isomer Shifts of  $\text{Np}(\text{III})$  Organometallics

Compound	Isomer Shift, $\text{cm/sec}^a$	Quadrupole Coupling Constant $eqQ/4$ , $\text{cm/sec}$	Reference
$\text{NpCp}_3 \cdot 3\text{THF}$	$3.65 \pm 0.10$		22
$\text{NpIn}_3 \cdot \text{THF}^b$	$3.55 \pm 0.10$		23
$\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$	$3.92 \pm 0.10$	$0.75 \pm 0.10$	26
$\text{NpCl}_3$	3.54		8

<sup>a</sup>. referred to  $\text{NpAl}_2 = 0$ <sup>b</sup>. In = indenyl, 

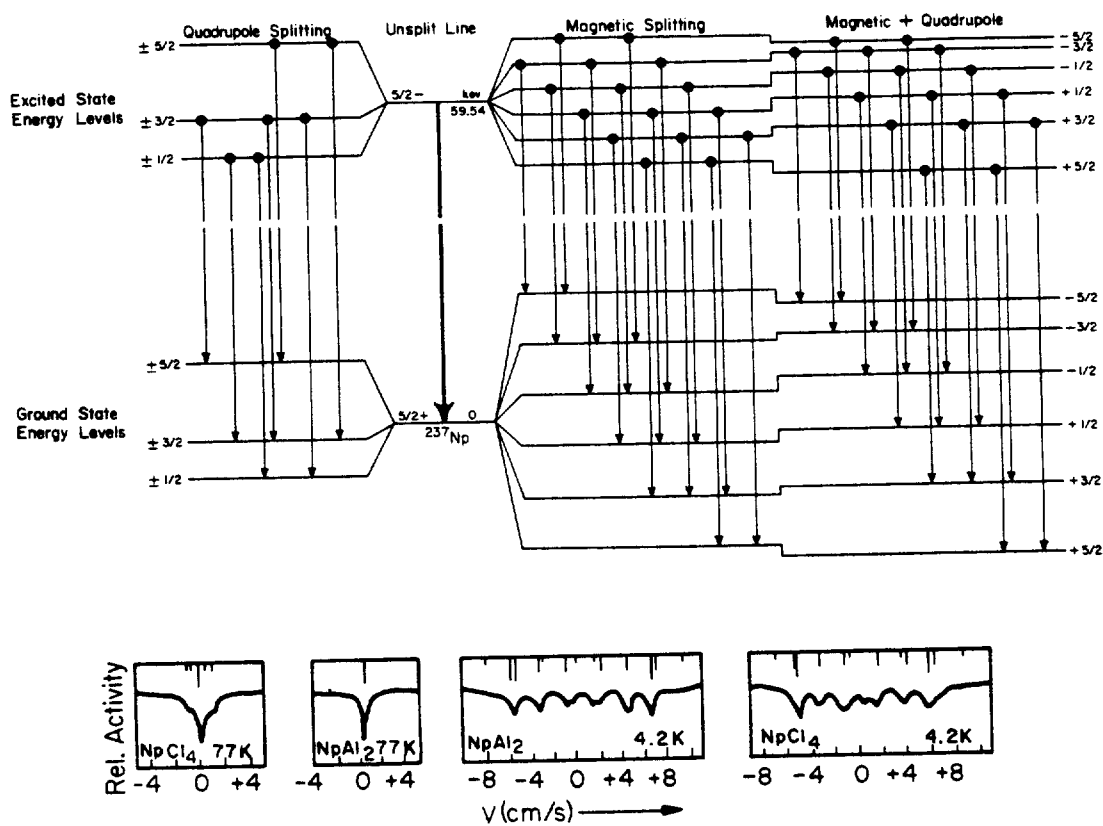


FIGURE 1. Splitting of the Ground State and 59.5 keV Level of  $^{237}\text{Np}$  in Magnetic and Electric Fields

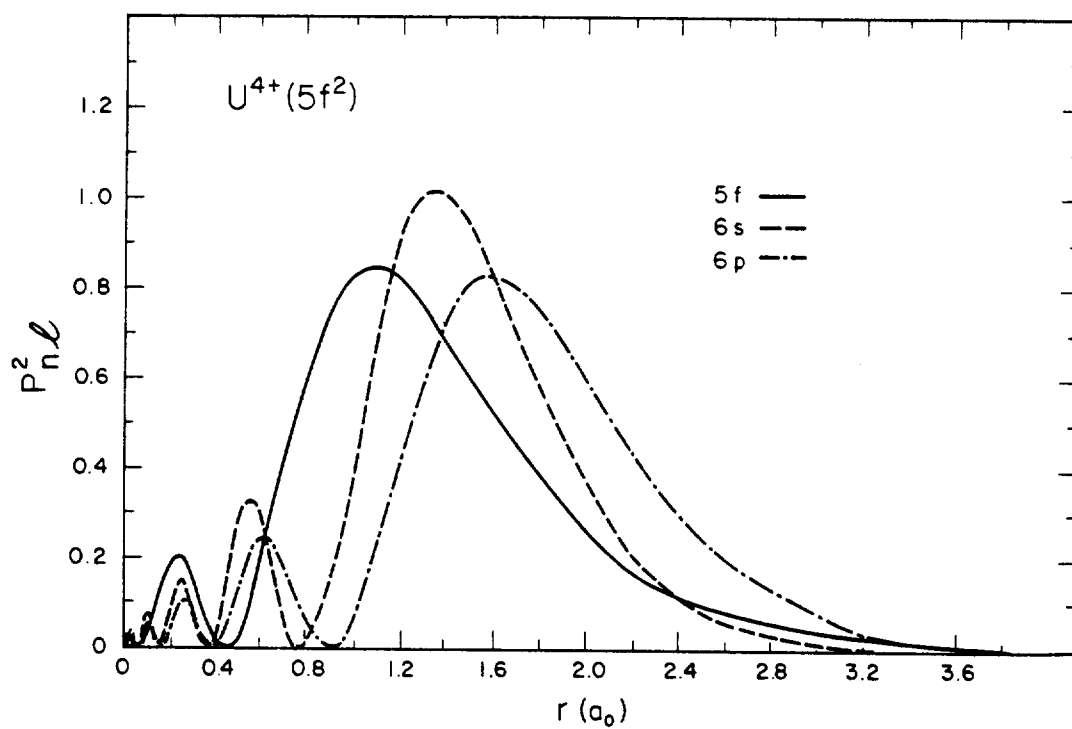


FIGURE 2. Radial Charge Density for  $U^{4+}$   
 (Courtesy of N.M. Edelstein, Lawrence  
 Berkeley Laboratory, Berkeley, CA)



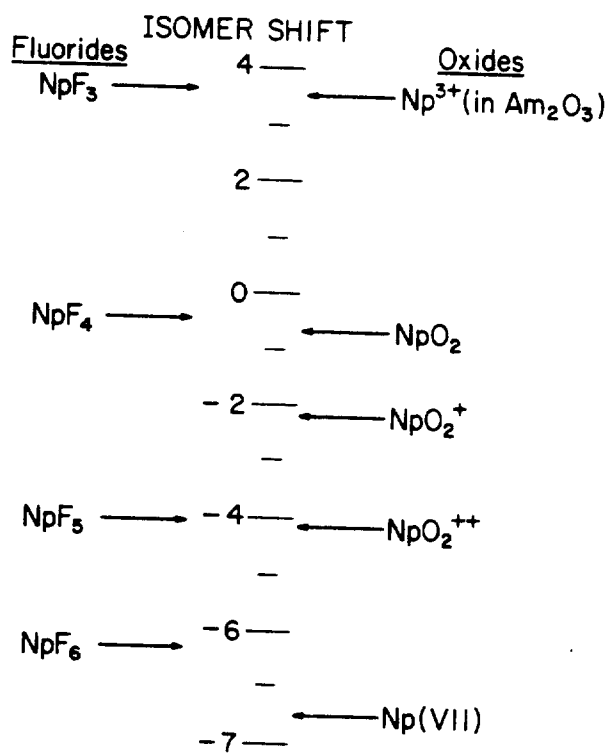


FIGURE 3. Isomer Shifts of Neptunium Fluorides and Neptunium Oxides

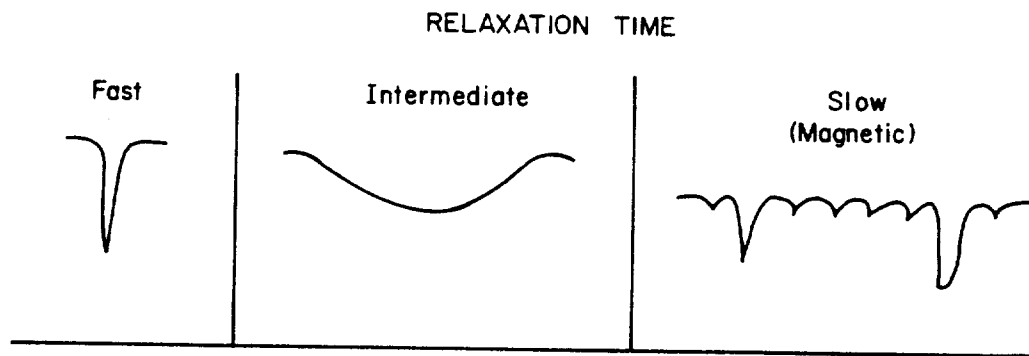


FIGURE 4. Relaxation Effects on  $^{237}\text{Np}$  Mössbauer Spectra

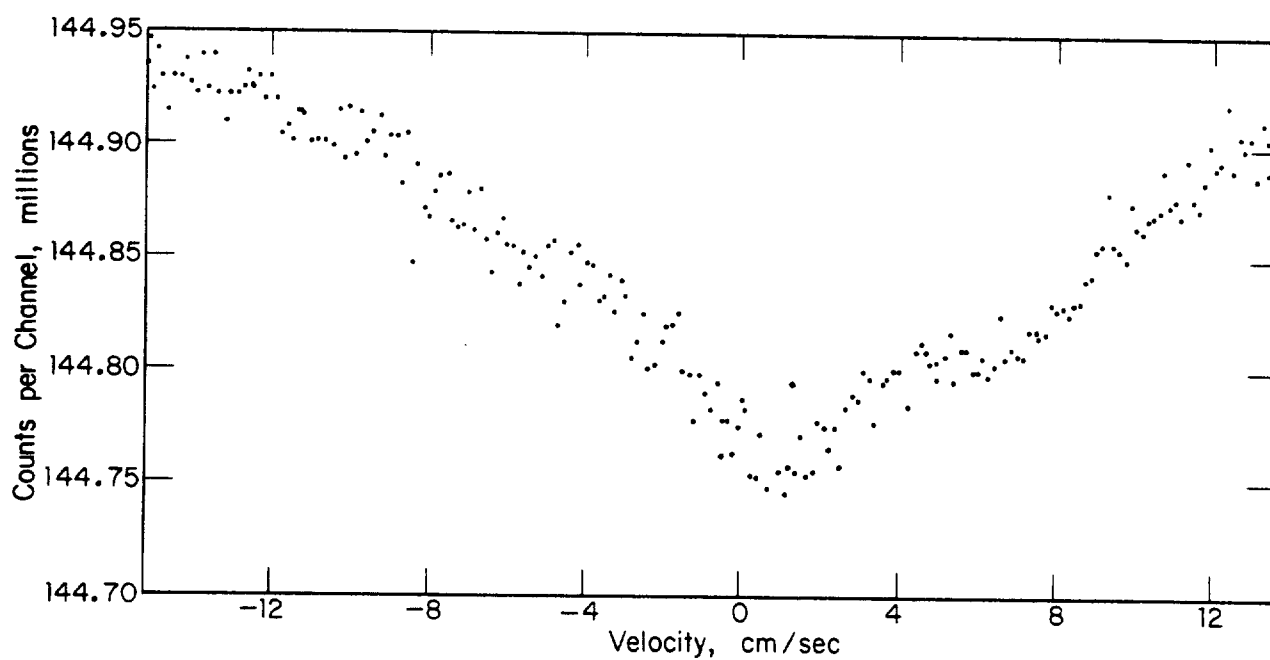


FIGURE 5. Mössbauer Spectrum of  $\text{Np}(\text{MeCp})_3\text{Cl}$

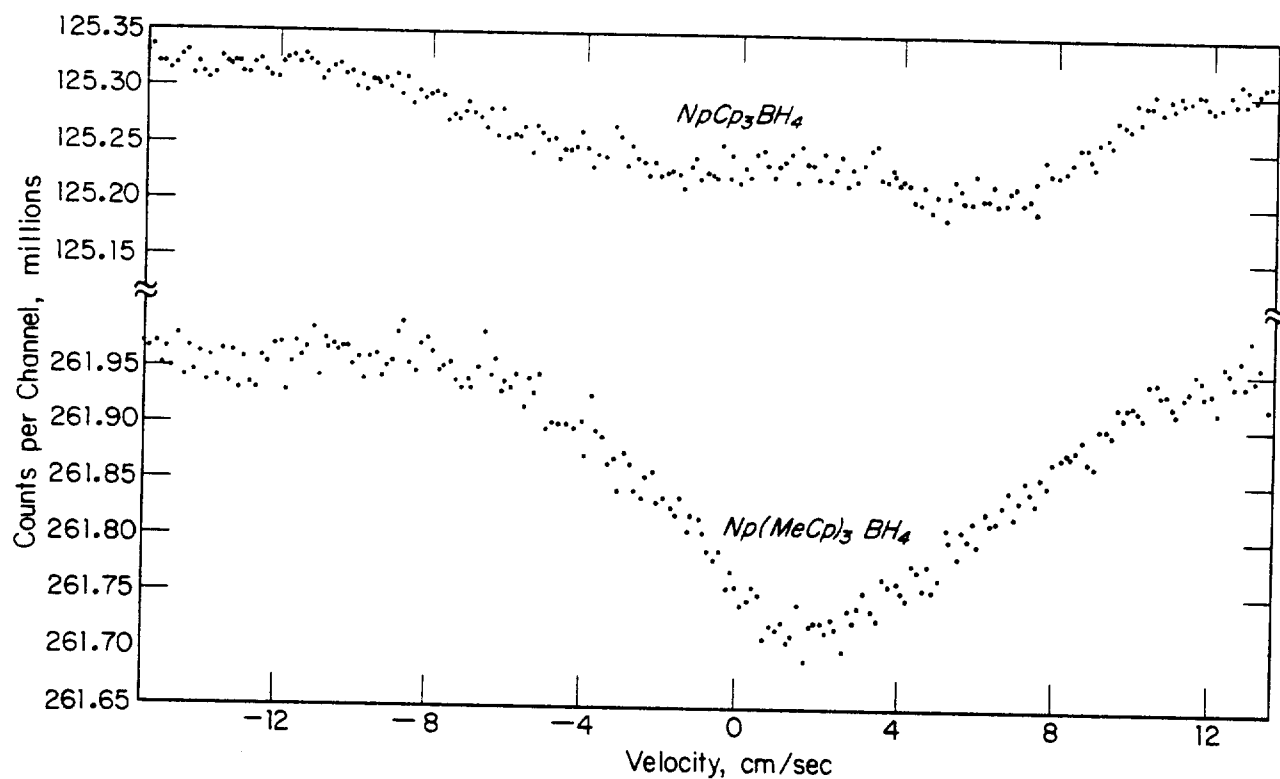


FIGURE 6. Mössbauer Spectra of  $\text{NpCp}_3\text{BH}_4$  and  $\text{Np}(\text{MeCp})_3\text{BH}_4$

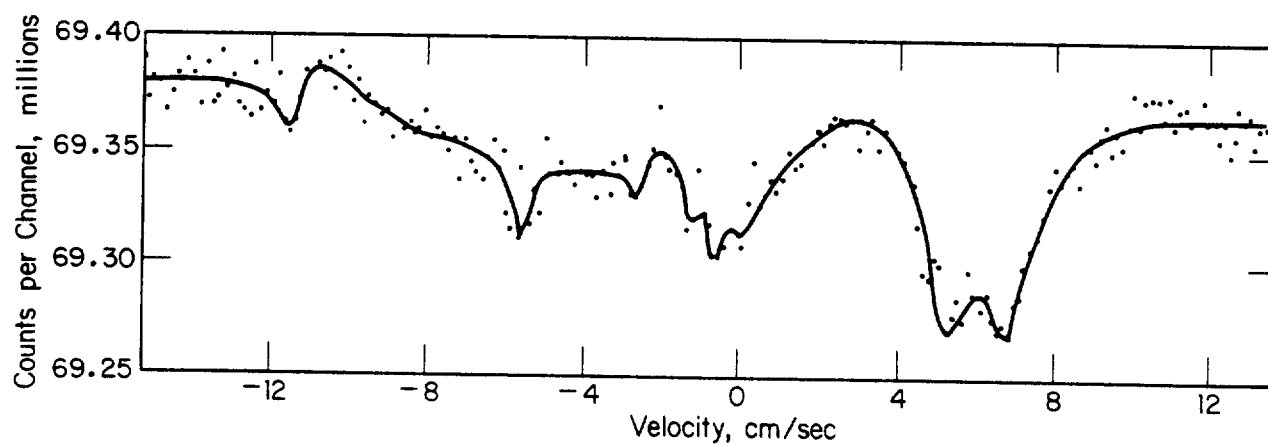


FIGURE 7. The Mössbauer Spectrum of  $\text{NpCp}_3\text{OCH}(\text{CH}_3)_2$

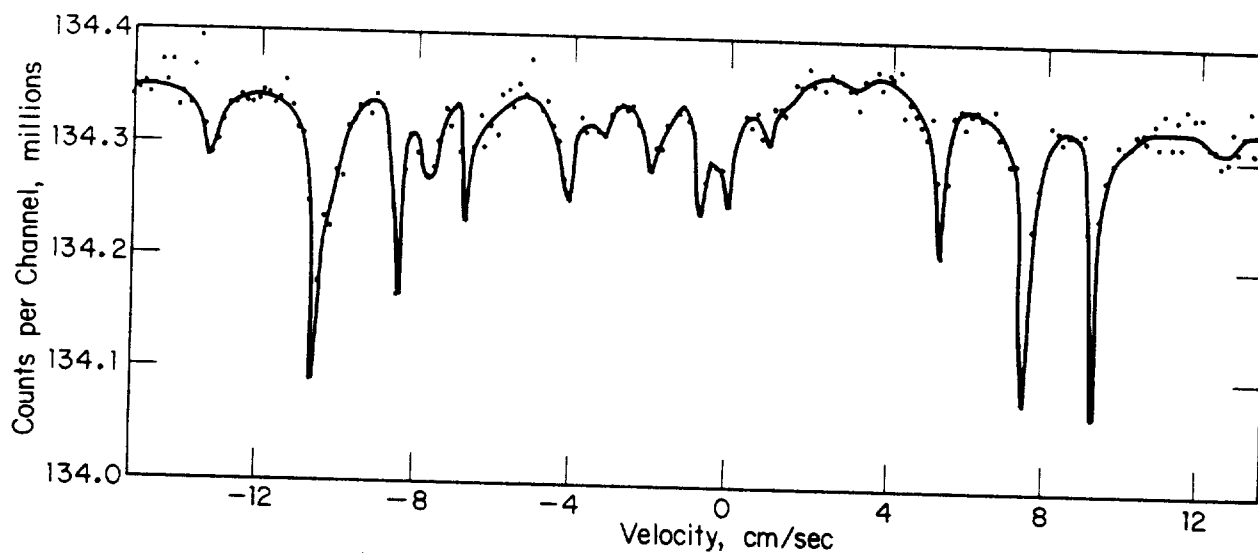


FIGURE 8. Mössbauer Spectrum of  $\text{Np}(\text{acac})_2\text{Cl}_2 \cdot \text{THF}$

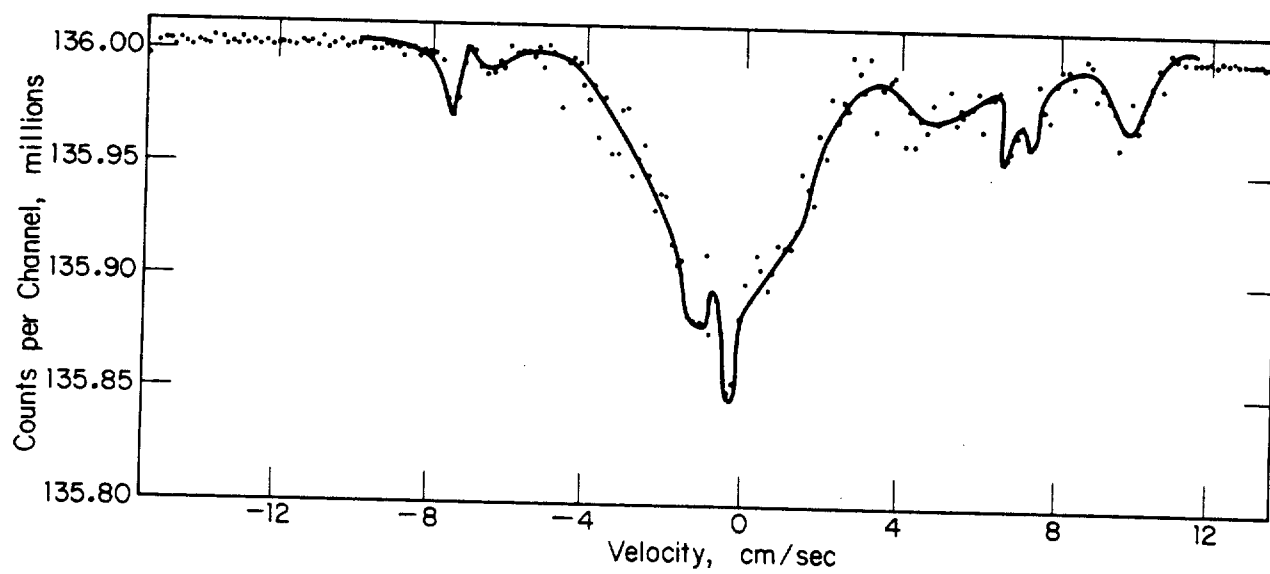


FIGURE 9. Mössbauer Spectrum of  $\text{Np}(\text{acac})_2(\text{MeCp})_2$