A ^{125}Te AND ^{129}I MÖSSBAUER STUDY OF

COMPLEXES OF TELLURIUM WITH THIOUREA

AND RELATED DERIVATIVES

by

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B.Sc., Simon Fraser University, 1970

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in the Department

of

Chemistry

March 1972

APPROVAL

Name: Robert Micheal Cheyne

Degree: Master of Science

Title of Thesis: A ^{125}Te and ^{129}I Mössbauer Study of Complexes

of Tellurium with Thiourea and Related

Derivatives

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Date Approved: 7 April 1972

(ii)

ABSTRACT

The ^{125}Te Mössbauer absorption spectra were recorded for a number of complexes of tellurium with thiourea, ethylenethiourea and tetramethylthiourea along with tellurium tetrakis(diethyldithiocarbamate) and tellurium dimethyl diiodide. The parameters obtained were interpreted in terms of the tellurium 5s and 5p orbital populations. The ^{129}I Mössbauer absorption spectra of cis-Te(tu)$_2$I$_2$ and trans-Te(etu)$_2$I$_2$ were also measured as a further check of the analysis of the ^{125}Te data.

The ^{129}I Mössbauer emission spectra of a number of ^{129m}Te labelled thiourea compounds were measured and evidence for the formation of the I-S bond in the ^{129}Te → ^{129}I radioactive decay was observed.

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I. INTRODUCTION

A. Purpose of the Present Study

The purpose of this work was to study chemical bonding and the effects of radioactive decay in some tellurium compounds by the use of Mössbauer spectroscopy. The study of the bonding involved the use of ^{125}Te and ^{129}I Mössbauer absorption spectroscopy while the study of the effects of radioactive decay was made by using ^{129}I Mössbauer emission spectroscopy.

The compounds that were chosen for this study were, for the most part, Te(II) and Te(IV) thiourea compounds which provide a series of compounds in which sulphur and halogen atoms are co-ordinated to a central tellurium atom in a number of different geometries. With the exception of a brief note [1] which appeared while the present work was being completed, the ^{125}Te Mössbauer parameters of the compounds of the present work have not previously been reported. The structures of these compounds have been relatively well established and thus the ^{125}Te Mössbauer parameters obtained will establish characteristic values for these geometries and oxidation states of tellurium.

The emission experiments were carried out with the principle aim that novel compounds with iodine-sulphur bonds could perhaps be prepared in radioactive decay and their bonding and structure studied through their Mössbauer emission spectra.

B. ^{125}Te Mössbauer

1. Features of the transition

Nuclear resonance absorption of the 35.48 keV. γ-ray from the 1.6 nanosecond excited state of ^{125}Te was first reported by Shpinel [2] and Shikazano [3]. The relatively short half-life of this state leads to a large Heisenberg width of the resonance profile of 2Γ = 5.32 mm. sec.$^{-1}$, but nevertheless measurable quadrupole splittings and isomer shifts are observed. The 35.48 keV. ^{125}Te excited state can be populated in the isomeric transition of ^{125m}Te, in the β^{-} decay of ^{125}Sb, and in the electron capture decay of ^{125}I, as shown in Figure 1. The transition to the ^{125}Te ground state is M1 with less than 1% electric quadrupole admixture, and is highly internally converted (α_T = 12.7).

2. Interpretation of the isomer shift

The nuclear isomer shift is defined as the displacement from zero velocity of the centroid of the Mössbauer resonance spectrum. This shift arises from the electrostatic interaction between the charge distribution for the nucleus and for those electrons which have a finite probability of being found within the region of the nucleus. The isomer shift in fact represents the difference between this interaction in the source compound and that in the absorber. Since, except for high z elements, only s electrons have a finite probability of being found within

$^{125}_{51}Sb$ 2.7 YR.

β^-

$\sigma = 5$ b.

$^{125m}_{52}Te$ 58 DAY ———— 0.145 MeV

E.C. $^{125}_{53}I$ 60 DAY

$^{124}_{52}Te$

$\frac{3}{2}+$ ———— 0.0355 MeV 1.6 nsec.

$\frac{1}{2}+$

$^{125}_{52}Te$
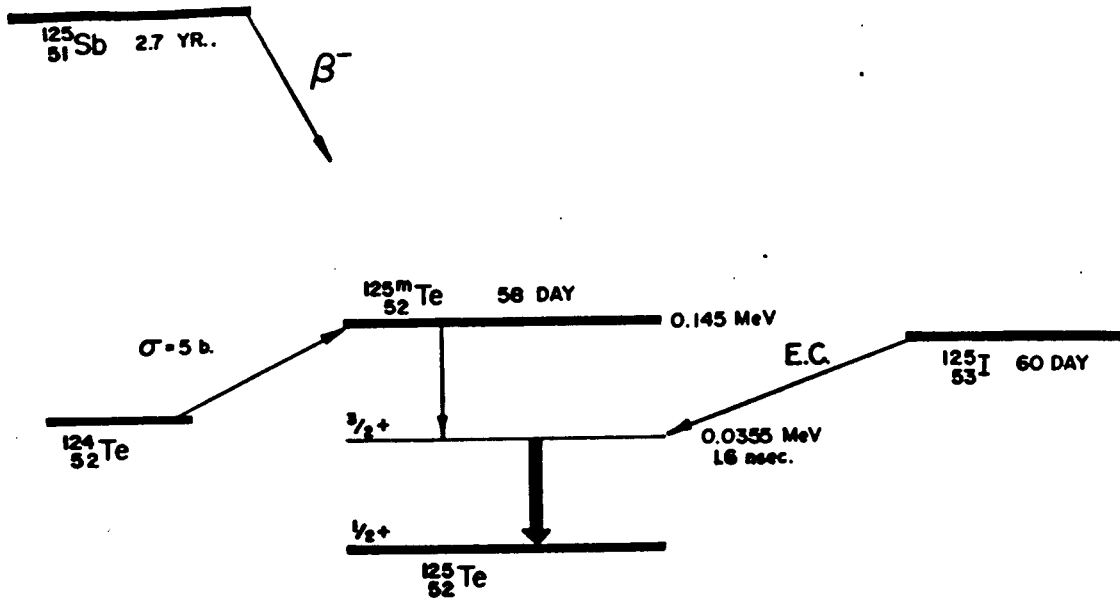
Figure 1.

Decay Scheme Showing the Population of the Mössbauer Transition
in ^{125}Te

$\pm\frac{3}{2}$

$I = \frac{3}{2}$

$\pm\frac{1}{2}$

$I = \frac{1}{2}$ $\pm\frac{1}{2}$
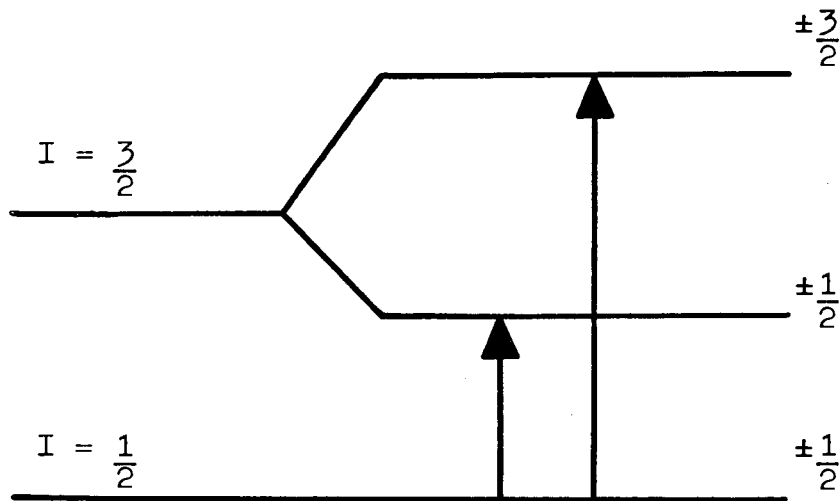
Figure 2.

^{125}Te Quadrupole Splitting

the nuclear volume, the isomer shift δ can be described by Equation 1.[4]

$$\delta = \text{constant}\ \frac{\Delta R}{R}\ [\ |\Psi s(o)|_a^2\ -\ |\Psi s(o)|_s^2\ ] \tag{1}$$

where R is the radius of the nucleus in the ground state, ΔR is the difference between the radius of the nucleus in the ground and excited states, and $|\Psi s(o)|^2$ "a" and "s" refer to the s-electron density at the nucleus in the absorber and source respectively.

From this expression we can see that to be able to interpret isomer shift values the sign of $\frac{\Delta R}{R}$ must be established. For ^{125}Te there has been some dispute on this point [5], but it is now generally agreed [6] that $\frac{\Delta R}{R}$ ^{125}Te is positive. Thus a positive isomer shift in a ^{125}Te absorption experiment indicates that a higher s electron density exists at the nucleus in the absorber than in the source.

All the compounds whose ^{125}Te Mössbauer spectra have previously been reported are listed in Table I. From this table we can see that the majority of the work in ^{125}Te Mössbauer Spectroscopy which has been carried out to date has been on the metal tellurides, the tellurium oxygen compounds and the tellurium halogen compounds.

If we examine the δ values in Table I we can see that the tellurium oxygen compounds, with the exception of TeO_2, exhibit

TABLE I

PREVIOUSLY REPORTED ^{125}Te MÖSSBAUER PARAMETERS

	*δ(mm. sec.$^{-1}$)	Δ(mm. sec.$^{-1}$)	REF.
H_6TeO_6	-1.29 ±.09 -1.23 ±.06 -1.15 ±.04 -1.20 ±.05		7 5 8 9
$(H_2TeO_4)_n$	-1.20 ±.05		7
α-TeO_3	-1.01 ±.07 -1.07 ±.05 -1.09 ±.02		7 8 9
β-TeO_3	-1.18 ±.07 -1.20 ±.02 -1.3 ±.2		7 9 10
TET.-TeO_2	+ .74 ±.11 + .72 ±.02 + .84 ±.12 + .72 ±.07 + .78 ±.08	6.76 ±.09 6.63 ±.06 6.25 ±.03 6.54 ±.08 7.3 ±.1	7 9 5 8 10
H_2TeO_3	+ .63 ±.34	6.71 ±.29	7
Na_2TeO_3	+ .35 ±.29 + .22 ±.05 + .16 ±.07	6.65 ±.16 5.78 ±.08 6.63 ±.06	5 8 9
$BaTeO_3$	- .47 ±.38	6.28 ±.20	5
$Na_2TeO_4 2H_2O$	-1.02 ±.07 -1.02 ±.02 - .99 ±.03		5 9 8
K_2TeO_4	- .98 ±.05 - .94 ±.08		8 5
$Na_2H_4Te(OH)_6$	-1.13 ±.02		9
$BaH_4Te(OH)_6$	- .94 ±.09		5

TABLE I

	*δ(mm. sec.$^{-1}$)	Δ(mm. sec.$^{-1}$)	REF.
Te METAL	+ .50 ±.05 + .78 ±.10 + .51 ±.04	7.72 ±.11 7.10 ±.11 7.4 ±.2	7 8 11
ZnTe	- .16 ±.04		8
CaTe	- .14 ±.07		5
PbTe	- .15 ±.1		5
$TeCl_4$	+1.0 ±.3 +1.2 ±.1	6.0 ±.3 4.0 ±1.6	12 8
$TeBr_4$	+1.1 ±.2 +1.1 ±.1	2.8 ±.2 3.8 ±4.0	12 8
TeI_4	+1.0 ±.2 +1.8 ±.9 +1.0 ±.6	2.7 ±1.0 ~4 6.0 ±1.0	12 8 11
$(NH_4)_2TeCl_6$	+1.7 ±.1 +1.63 ±.05 +1.88 ±.05		12 13 5
Rb_2TeCl_6	+1.88 ±.04		5
$(NH_4)_2TeBr_6$	+1.4 ±.1 +1.66 ±.04		12 5
Rb_2TeBr_6	+1.65 ±.04		5
$(NH_4)_2TeI_6$	+1.1 ±.1 +1.14 ±.08 +1.47 ±.09		12 13 5
Rb_2TeI_6	+1.46 ±.08		5
NH_4TeF_5	+1.09 ±.33	5.85 ±.09	5
$Te(SCN_2H_4)_4Cl_2$	+1.49 ±.5	16.5 ±.8	1

TABLE I

	*δ (mm. sec.$^{-1}$)	Δ (mm. sec.$^{-1}$)	REF.
Te(SCN$_2$H$_4$)$_2$Cl$_2$	+1.49 ±.5	16.5 ±.8	1
Te(C$_{12}$N$_2$S$_3$)$_4$	+ .5 ±.3	13.0 ±.5	1

* δ is measured in this table with respect to a ^{125}I on copper source.

large negative isomer shifts, indicating a low s-electron density
at the nucleus. On the other hand, the tellurium halogen compounds
exhibit large positive values, indicating a high s-electron
density at the nucleus. Also, the isomer shifts of the TeX_6^{2-}
compounds, and thus the s-electron density at the nucleus in
these compounds, increase with the increasing electronegativity
of the halogen. These observations have been interpreted in the
following manner [5]. In the TeX_6^{2-} $(5s^2\ 5p^0)$ compounds the
lone pair is assumed to occupy the non-stereochemically active
5s orbital, while the six Te-X bonds are formed through the
p_x, p_y and p_z orbitals. Then, with the increasing electronegativity
of the halogen an increasing number of p electrons will be
withdrawn from the central tellurium atom. This will decrease the
shielding of the 5s electrons from the nucleus by the 5p electrons,
and will thus increase the isomer shift. In the tellurium-oxy
compounds which have negative isomer shifts, however, some s
hybridization must be present in the bonding orbitals. Here it
is proposed that the highly electronegative oxygen ligands are
withdrawing both s and p electrons from the central tellurium,
resulting in a net decrease in the isomer shift. It is evident
from this that the direct removal of s electrons has a more
pronounced effect on $|\psi s(o)|^2$ than does the removal of p electrons.

This theory of pure p bonding in the TeX_6^{2-} compounds
is also supported by evidence other than the Mössbauer data. The
Raman spectra of these compounds [14] show the Te-X bonds to be

weak interactions as would be expected when two ligands are bonded through one p orbital on the tellurium. Also, the fact that these compounds are octahedral [15] indicates that the lone pair must be occupying the non-stereochemically active 5s orbital. Couch et al.'s interpretation of the electronic spectra of these compounds, [16] however, indicates that the 5s electrons may not be totally spectroscopically "inert" as some relatively low energy transitions are observed which apparently involve them. On this evidence they state that the $5s^2$ electrons are partially delocalized to the ligands. However no conclusion was arrived at as to the extent of this apparent delocalization. It may be concluded that the bonding in the TeX_6^{2-} anions occurs predominantly through the tellurium 5p orbitals and that any participation by the 5s orbitals must be very small.

In a further developement of this concept, a relationship has been derived[12] between the ^{125}Te isomer shift and the charge on the tellurium atom. Making the assumption that the tellurium atom uses only 5p-orbitals in bonding it was concluded that

$$\delta \; (^{125}Te) = 0.45 \pm 0.01 \; hp - 0.15 \pm 0.03 \tag{2}$$

where δ is the ^{125}Te isomer shift in mm. sec.$^{-1}$ with respect to an ^{125}I on copper source and hp is the number of 5p electrons which have been removed from the closed shell $5p^6$ configuration of an ionic Te^{2-} ion. The charges on the tellurium atom in the TeX_6^{2-} anions were calculated from the halogen Nuclear Quadrupole Resonance data [17] for the tellurium hexahalides using Townes

and Dailey's theory.[18]

3. Interpretation of the Quadrupole Splitting

The quadrupole splitting in a Mössbauer spectrum is the
result of the interaction of the nuclear quadrupole moment Q,
with the gradient of the electric field at the nucleus, where Q
is a measure of the deviation of the nucleus from spherical
symmetry. The electric field gradient can be completely described
by three components $\frac{\partial^2 V}{\partial x^2}$, $\frac{\partial^2 V}{\partial y^2}$ and $\frac{\partial^2 V}{\partial z^2}$ (generally abbreviated Vxx,

Vyy and Vzz). However these three components are not independent
since they must obey the Laplace equation in a region where the
charge density vanishes.

ie. Vxx + Vyy + Vzz = 0 . $\qquad\qquad$ (3)

As a result there remain only two independent components, usually
chosen as Vzz or eq and η, the asymetry parameter, defined by

$$\eta = \frac{Vxx - Vyy}{Vzz} \ . \qquad\qquad (4)$$

The allowed energy states which result from this interaction
between the electrostatic field gradient, q, and the nuclear
quadrupole moment are then given by Equation 5. [4]

$$E_Q = \frac{e^2qQ}{4I(2I-1)} \; [3m_I^2 - I(I+1)](1 + \frac{\eta^2}{3})^{\frac{1}{2}} \qquad (5)$$

where I is the nuclear spin and m is the z component of the nuclear spin. For levels with a spin of $\frac{3}{2}$, as in the [125]Te first excited state, this expression reduces to

$$\Delta = 2 \; E_Q = \frac{e^2qQ}{2} \; (1 + \frac{\eta^2}{3})^{\frac{1}{2}} \; . \qquad (6)$$

The interaction then lifts the spin degeneracy of the $I = \frac{3}{2}$ excited level as shown in Figure 2, where the interaction is positive if the $\pm \frac{3}{2}$ state of the excited level is higher than the $\pm \frac{1}{2}$ state, as given by Equation (5).

The nuclear quadrupole moment, Q, for [125]Te has not been experimentally measured, but calculations [19,20] have been carried out which arrive at a value for Q [125]Te of approximately 0.2 barns. Pasternak and Bukshpan [21] have also concluded that the sign of Q [125]Te is negative.

Almost all of the tellurium compounds whose Mössbauer parameters have been measured to date have been either octahedral, or polymeric with rather poorly defined or complex stereochemistry. As a result, essentially no interpretations of the [125]Te quadrupole splitting data have appeared in the literature, other than those of Violet et al.,[20] who attempted to describe the bonding in tellurium metal,and the discussion of tellurium metal

and TeO_2 by Pasternak and Bukshpan. [21]

4. Goldanskii - Karyagin Effect

In the case of a quadrupole split Mössbauer spectrum information can be obtained, not only from the magnitude of Δ, but also from the relative intensities of the peaks in the spectrum. If the quadrupole measurements are made with a single crystal for which it is possible to define the field gradient axis, a change in the intensities of the hyperfine components may be observed as the angle of incidence of the γ-radiation is altered. This angular correlation between the incident γ-radiation and the field gradient axis is due to the difference in polarization of the hyperfine interactions. For ^{125}Te the intensity ratio of the two transitions $(\pm \frac{3}{2} \to \pm \frac{1}{2})$ and $(\pm \frac{1}{2} \to \pm \frac{1}{2})$ will be given by: [20]

$$\frac{I_1 (\pm \frac{3}{2} \to \pm \frac{1}{2})}{I_2 (\pm \frac{1}{2} \to \pm \frac{1}{2})} = \frac{1 + \cos^2\theta}{\frac{5}{3} - \cos^2\theta} \qquad (7)$$

Where θ is the angle between the direction of γ-radiation and the electrostatic field gradient.

However in a polycrystalline sample, where an isotropic distribution of field gradients exists, the intensity of the two peaks would normally be equal, since Equation (7) integrated over all directions gives $I_1 = I_2$. However it has been shown by Goldanskii [23] that if the Mössbauer recoil free factor, f, is

anisotropic then

$$\frac{I_1}{I_2} = \frac{\int_0^\pi (1 + \cos^2\theta)\, f_{(\theta)}\, \sin\theta\, d\theta}{\int_0^\pi (\frac{5}{3} - \cos^2\theta)\, f_{(\theta)}\, \sin\theta\, d\theta} \neq 1 \tag{8}$$

and two peaks of differing intensities will be observed even for a polycrystalline sample. This effect has been used by Pasternak[21] to calculate the sign of Q ^{125}Te.

C. ^{129}I Mössbauer

1. Features of the Transition

The Mössbauer transiton in ^{129}I emanates from a 27.7 keV., 16.8 nanosecond level to the ^{129}I ground state. The relatively long lifetime of the excited state leads to a narrow natural line-width (2Γ = .59 mm. sec.$^{-1}$) and easily observable isomer shifts and quadrupole splittings result. The level can be populated in the β decay of ^{129}Te or ^{129m}Te as shown in Figure 3.

2. Interpretation of the Isomer Shift

As in the case for ^{125}Te, $\frac{\Delta R}{R}$ for ^{129}I is considered to be positive, [24] where a positive isomer shift in an absorption experiment will indicate a higher s-electron density at the absorbing nucleus than at the source nucleus.

If we examine the isomer shifts for a variety of ^{129}I
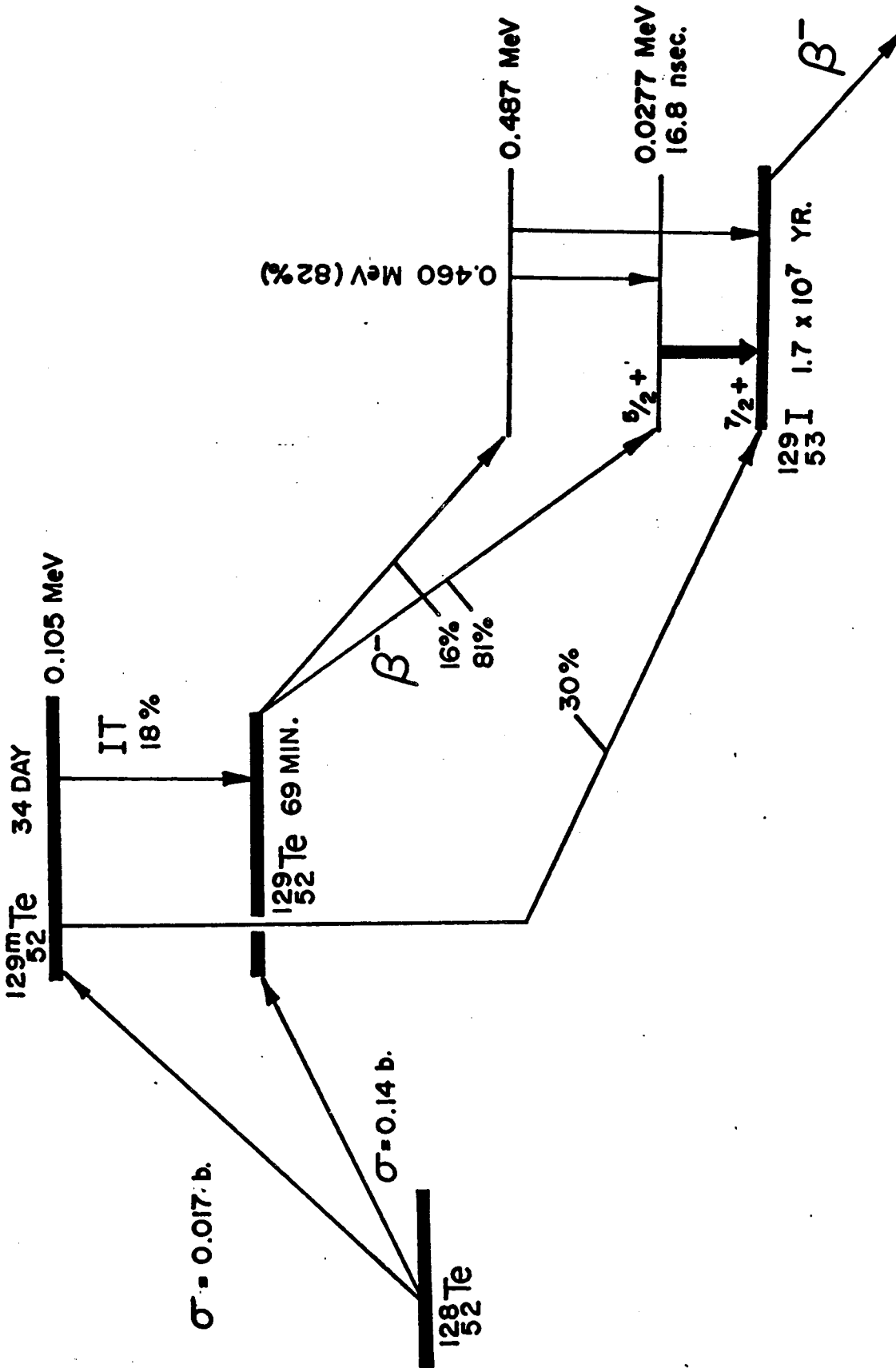
Figure 3.

Decay Scheme for ^{129m}Te and ^{129}Te.

absorbers as shown in Figure 4, we can see that for the iodine oxy- and fluoro-compounds large negative isomer shifts are observed, while for compounds with less electronegative ligands, such as the interhalogens (excluding fluorine) large positive isomer shifts are found. This is almost completely analogous to the situation found for ^{125}Te and is interpreted in the same manner. That is, the compounds with positive isomer shifts are assumed to be using only p orbitals in bonding, while the bonding orbitals in the compounds displaying negative isomer shifts are assumed to involve some s hybridization.

An expression relating the isomer shift to the electron "holes" in the 5p shell has been established for ^{129}I, assuming pure p bonding, by Bukshpan et al. [25]

$$\delta = 1.5 \text{ hp} - 0.54 \quad . \tag{9}$$

An expression involving the contribution to δ from s electrons has also been calculated [25] (Equation 10) assuming that IO_4^- and IO_6^- are sp^3 and sp^3d^2 hybridized, respectively.

$$\delta = -9.2 \text{ hs} + 1.5 \text{ hp} - 0.54 \quad . \tag{10}$$

In both Equations 9 and 10 δ is in mm. sec. $^{-1}$ measured relative to ZnTe.

The calculation of the ^{129}I isomer shift from the experimentally observed spectrum is complicated by the fact that
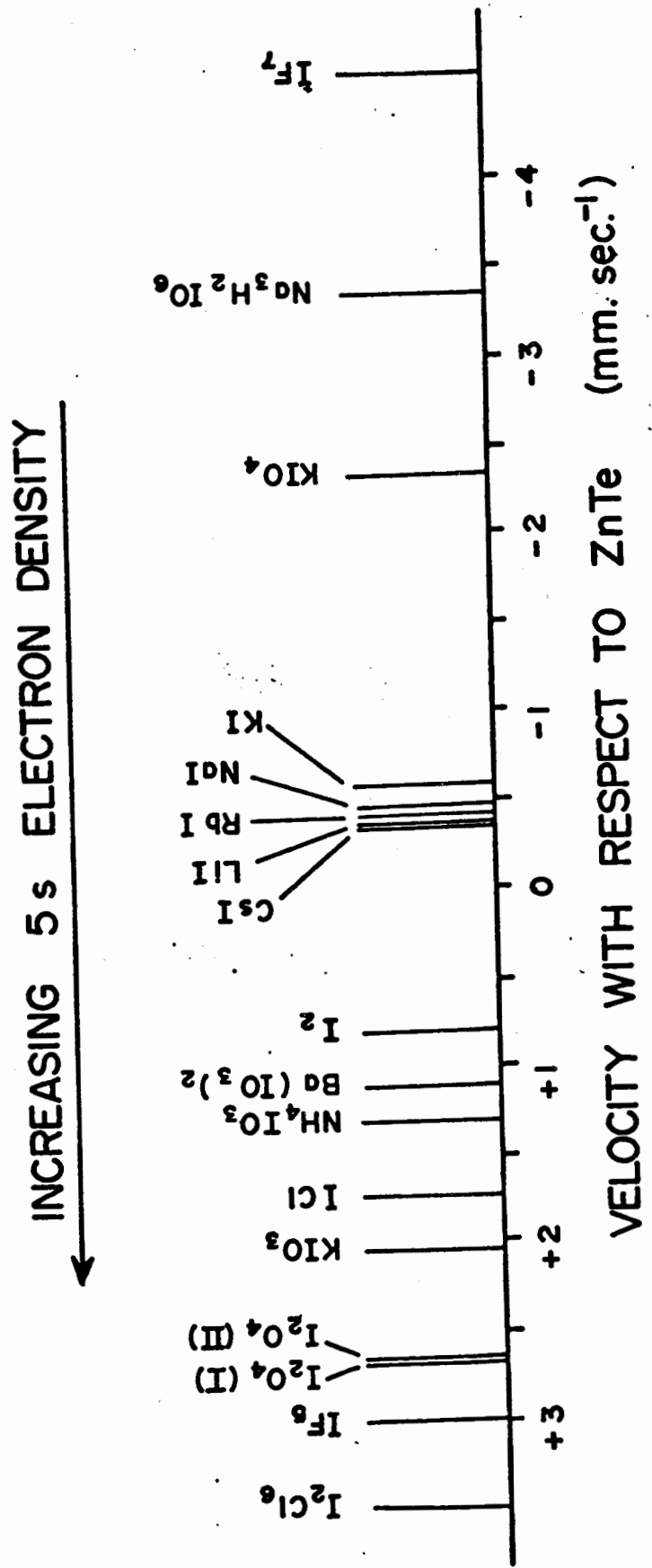
Figure 4.

A Comparison of Isomer Shifts for ^{129}I Labelled Compounds

the Mössbauer transition takes place from an excited state of spin $\frac{5}{2}$ to a ground state of spin $\frac{7}{2}$. As a result, when the nucleus is placed in a non-spherically symmetrical electrostatic field the ground and excited levels are split into 4 and 3 levels respectively and an eight line quadrupole split spectrum arises from the allowed transitions of $\Delta m = 0 \pm 1$ as shown in Figure 5.

An expression for the position of each line in a quadrupole split spectrum as a function of the isomer shift, assuming that only terms up to η^2 may be considered, has been derived.[26]

$$\delta_{ij} = \frac{ce^2 qQ_{gnd}}{4E_\gamma} \left[\frac{Q_{ex}}{Q_{gnd}} \frac{(C_o^* + C_2^* \eta^2)}{I^*(2I^* - 1)} - \frac{(C_o + C_2 \eta^2)}{I(2I - 1)} \right] + \delta \qquad (11)$$

where δ_{ij} is the position of the line corresponding to the $m_i \rightarrow m_j$ transition, δ is the isomer shift, $\frac{Q_{ex}}{Q_{gnd}} = 1.231 \pm .001$[27]

$$C_o = 3m^2 - I(I + 1) \qquad (12)$$

and

$$C_2 = \frac{1}{12} \left[\frac{f(I,m-1)}{m-1} - \frac{f(I,m+1)}{m+1} \right] \qquad (13)$$

where

$$f_{(I,m)} = \frac{1}{4} (I^2 - m^2) [(I - 1)^2 - m^2] \quad . \qquad (14)$$

Values of δ_{ij} have been calculated[28] for values of η from
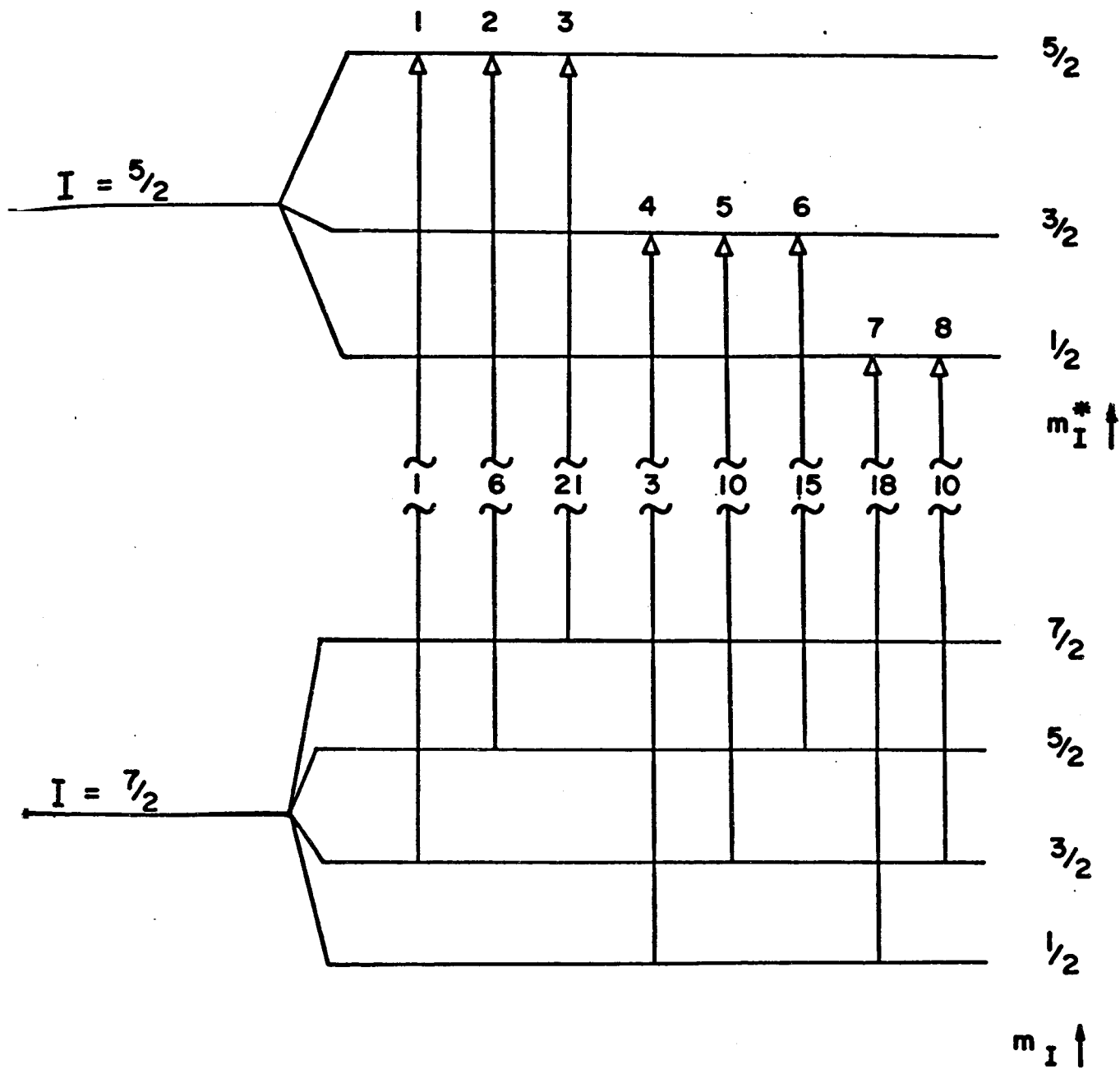
Figure 5.

^{129}I Quadrupole Splitting for e^2qQ_{gnd} Positive

0 to 1 as shown in Figure 6, where lines 4 and 8 are thus found to be the only two lines which are significantly η dependent. Thus the lines may be identified from their relative positions and also from their intensities which are proportional to the square of the Clebsh - Gordon coefficients[29]. The values of e^2qQ and δ are then found from any of the lines (except 4 and 8), usually by the least squares method, and η can then subsequently be determined from lines 4 and 8.

3. Interpretation of the Quadrupole Splitting

The quadrupole splitting in ^{129}I spectra can also be used to describe the electronic environment about the I atom in terms of p orbital populations. This is done by means of the theory of Townes and Dailey[18], which describes the origin of the electrostatic field gradient itself in terms of p orbital populations.

In this theory the principal axis of the molecule is defined as the z-axis and e^2qQ_{mol} the quadrupole coupling for the molecule of interest is defined as;

$$e^2qQ_{mol} = - U_p \, e^2qQ_{atom} \tag{15}$$

where e^2qQ_{atom} is the quadrupole coupling constant for one p electron, whose value for ^{129}I is 1607 Mc. sec.$^{-1}$,[30] and U_p, the p electron deficit or excess along the z-axis, is
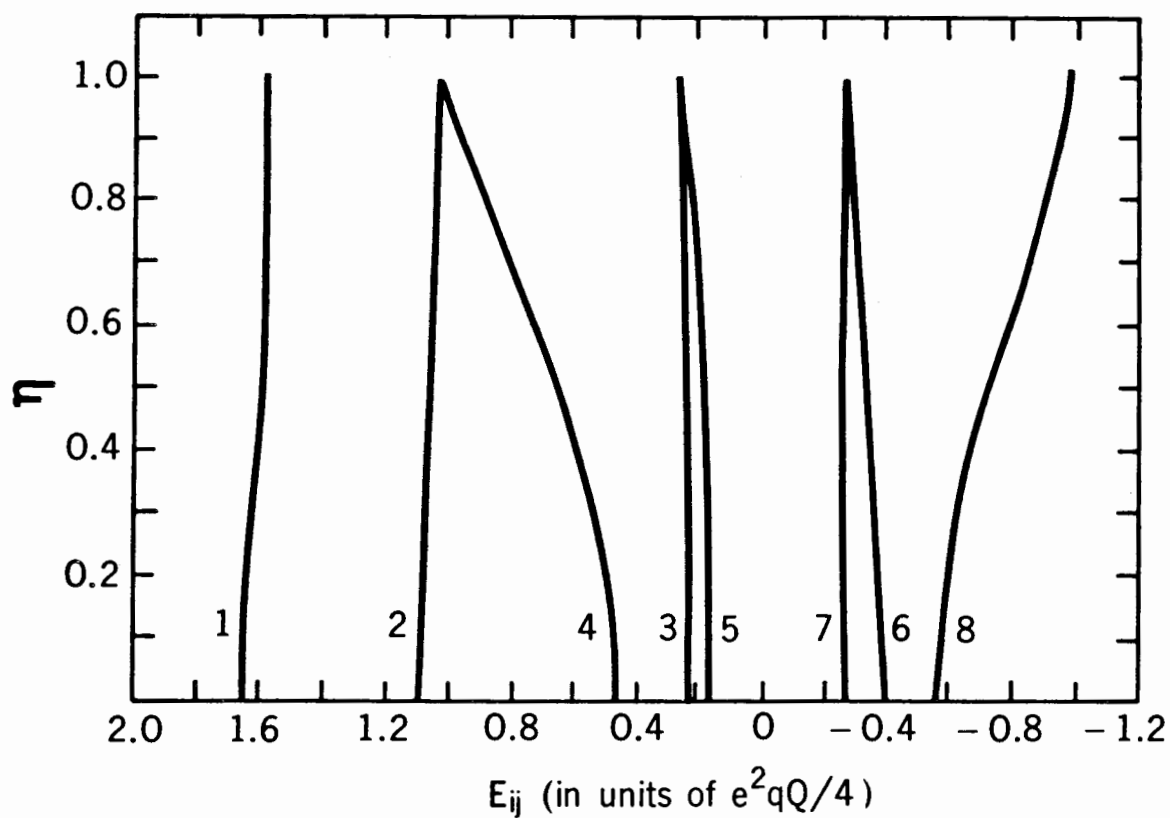
FIGURE 6   Dependance of the energy positions E_{ij} on η
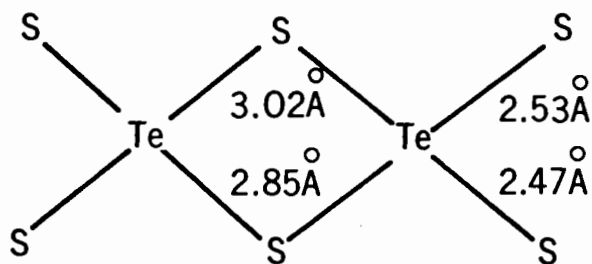
FIGURE 7   Structure of $Te(tu)_3(HF_2)_2$

defined by;

$$Up = -Uz + \frac{(Ux + Uy)}{2} \qquad (16)$$

where Ux, Uy, and Uz are the electron populations in the x,y, and z directions. The asymmetry parameter η which defines the divergence from axial symmetry in the molecule is then given by;

$$\eta = \frac{3}{2} \frac{Ux - Uy}{Uz} \quad . \qquad (17)$$

Thus since hp can be expressed as

$$hp = 6 - (Ux + Uy + Uz) \qquad (18)$$

it is possible to determine values of Ux, Uy, and Uz from δ, η and e^2qQ. The relationship between hp and Up can also be used as an independent check of the p-bonding model. Thus, making the assumption that only p orbitals are involved in bonding, for the case of

(1) a linear I-Ligand bond

$$hp = Up \qquad (19)$$

(2) a square planar IL_4

$$hp = 2Up \qquad\qquad (20)$$

These relationships have been found by Pasternak et al.[31] to hold for ICl (linear bond) and I_2Cl_6 (approximates a square plane of chlorine atoms about the I). Deviations from equations 19 and 20 may be a result of π bonding, as in the case of SnI_4[32] or s hybridization, as in $Na_3H_2IO_6$, KIO_4 and the $CH_{4-n}I_n$[33] series.

D. ^{129}I Emission Mössbauer Spectroscopy

1. Chemical Effects of Radioactive Decay

When an atom which is chemically bound in a molecule undergoes a nuclear transformation, the daughter atom thus formed may be observed to have broken some or all of its original chemical bonds. This molecular distruption may occur as a result of recoil kinetic energy acquired by the daughter mucleus as a consequence of momentum conservation, or as a result of electronic excitation or ionization produced by the nuclear transformation.[34] In our study we will be concerned with the chemical effects accompanying the β^- decay $^{129}Te \xrightarrow{\beta^-} {}^{129}I$ and the isomeric transition $^{129m}Te \rightarrow {}^{129}Te$ and a brief discussion of the processes accompanying these two types of decay follows.

In ^{129m}Te the isomeric transition to ^{129}Te takes place by the emission of an orbital electron (internal conversion) in all events. This leads to a process known as Auger charging. In this process, the inner-shell hole left by the internal conversion

event is filled by an electron from an outer shell and the difference

in binding energy between the electrons in those two shells is

either emitted as an x-ray, or is given to a second outer shell

electron which is then also ejected from the atom. This latter

process leads to a multiplication of the number of holes as the

initial hole moves out to the periphery of the atom, and results

in the creation of a very high charge on the atom in a time of

ca. 10^{-14} second following the internal conversion event.

For example, in the gas phase following the highly

internally converted isomeric transiton $^{131m}Xe \rightarrow ^{131}Xe$, the xenon

ions are distributed in charge from +1 to +23 with a most probable

charge of +8. Moreover, molecules undergoing this process in the

gas phase are found to virtually explode[34]due to coulombic

repulsion between the positively charged centres produced in the

molecule.

In the solid state however it would be expected that

rapid charge neutralization would occur as electrons are transferred

back to the excited atom from the surrounding lattice even as

the Auger cascade itself is moving to the outer shells of the atom.

Thus,very high charge accumulation may be prevented in a solid

lattice. This, along with the constraining effects of the

surrounding atoms and molecules, would be expected to reduce the

amount of molecular disruption accompanying the decay event in the

solid state.

In β^- decay, an electron of high kinetic energy and an

antineutrino are ejected spontaneously from the nucleus of the

radioactive atom. In order that momentum be conserved in a β^-
decay, the decaying atom must recoil. However, in the decay
$^{129}Te \xrightarrow{\beta^-} {}^{129}I$ the energy of the β^- particle is relatively small
and hence a very low recoil energy is imparted to the nucleus
and no molecular disruption would be expected to result.
Moreover, electronic excitation which may occur as a result of β^-
decay is found to be very small, and charge spectra obtained for
the rare gases at low pressures have been found to show the
occurrence of a charge of +1 in 80 to 90 percent of events.
In general, far less molecular disruption is found in gases
following β^- decay[34] than following internal conversion.

In Mössbauer emission experiments a radioactive nuclide
bound in a molecule is used to populate the Mössbauer transition which
yields information on the electronic structure of the newly
formed molecule nanoseconds after it has been formed in the
crystal. Thus Mössbauer Spectroscopy is a very useful tool for the
study of the chemical effects of radioactive decay in solids.

2. A Review of Past Investigations; Interpretation of the
   Isomer Shift and Quadrupole Splitting

Of the compounds studied to date, by ^{129}I emission
Mössbauer, some have shown molecular decomposition following
the radioactive decay, while others have appeared to remain
intact, the daughter atom being found in a lattice environment
isoelectronic and isostructural with that of the parent.[35,36,38]
The results of these previous experiments may be illustrated with
reference to several specific examples.

Telluric acid, H_6TeO_6, contains Te^{VI} octahedrally co-ordinated to six-OH groups. When $Te(OH)_6$ is labelled with ^{129}Te and the ^{129}I Mössbauer emission spectrum is recorded against a $Na^{129}I$ absorber,[36] it is observed that following the $^{129}Te \rightarrow {}^{129}I$ β^- decay, the iodine remains bonded to the six oxygens. This is evidenced by a single line in the Mössbauer experiment with an isomer shift analogous to that observed in $Na_3H_2IO_6$[37] in an absorption experiment. In contrast, when the Mössbauer emission sectrum of $H_6{}^{129m}TeO_6$ is studied, a more complex spectrum results in which a second iodine molecule is also observed. It is apparent that in the $^{129m}Te \rightarrow {}^{129}Te$ isomeric transition, which is highly internally converted, ca. 50% of the tellurium atoms break their parent bonds and are reduced to Te^{IV}. In the subsequent β^- decay and Mössbauer transition, two iodines are then identified, one a single line of isomer shift corresponding to IO_6^{5-} and the other a quadrupole split species with a quadrupole coupling and isomer shift similar to that of IO_3^-. The tellurium precursors formed in the isomeric transition are presumably H_6TeO_6 and TeO_3^{2-}[36]. Thus in this instance the Mössbauer effect is being employed as a probe to study the effects of the isomeric transition in the solid state.

A second example is the study of the tellurium hexahalide ions. Here it is observed that when NH_4TeCl_6 is labelled even with ^{129m}Te the principle Mössbauer emission corresponds to that of the $^{129}ICl_6^-$ ion, indicating that the radioactive decay has not

brought about extensive molecular decompostion.[39] In contrast
^{129m}Te and ^{129}Te-labelled $TeCl_4$ were observed to yield the same

complex emission spectrum which indicated that in this case very

extensive molecular rearrangement accompanied the decay, and that

this rearrangement was not brought about by the isomeric

transition.[12] It is apparent that electronic excitation

accompanying the radioactive decay is not the only factor which

results in molecular rearrangement but that the chemical stability

of the daughter molecule is also of importance.

The Mössbauer absorption and emission studies of

the tellurium-oxygen compounds and the hexahalides have also

allowed the determination of the ratio of ^{125}Te and ^{129}I isomer

shifts and quadrupole coupling constants for tellurium and iodine

in isoelectronic and isostructural environments. Thus it has

been found[12] that

$$\frac{\delta(^{125}Te)}{\delta(^{129}I)} = +0.29 \pm .01 \tag{21}$$

where δ is measured relative to ZnTe for both isotopes and

$$\frac{e^2qQ^{125}Te\ (1 + \frac{\eta^2}{3})^{\frac{1}{2}}}{e^2qQ^{129}I} = 0.45 \pm .01 \tag{22}$$

It should be noted that standard absorption experiments do not allow a ready determination of these ratios because of the absence of conventionally preparable tellurium and iodine molecules which are isostructural and isoelectronic.

In the present study the Mössbauer emission spectra of ^{129m}Te labelled thiourea complexes were studied to determine if in radioactive decay novel compounds containing I-S bonds would be observed.

E. Review of Some Tellurium Compounds

1. Tellurium Thiourea Compounds

Foss[40] has undertaken a detailed x-ray crystallographic structural study of the compounds of tellurium with thiourea and its related derivatives. The six structural types of compounds which have been identified are shown in Table II and a discussion of the structural data obtained on each type follows.

(a) $Te^{II}L_4X_2$
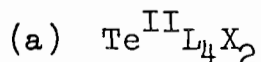
X-ray crystal structure determinations have been carried out on $Te(tu)_4Cl_2$, $Te(tu)_4Cl_2 \cdot 2H_2O$[41] and $Te(etu)_4Cl_2$.[42] In all cases a TeL_4^{2+} square planar cation was observed with Te-S bond lengths of $2.69 \pm .01$Å and S-Te-S bond angles of $90°$, within the error of the measurement. The Te-Cl contacts were found to be longer than the sum of the Van der Walls radii of 4.00 Å. Preliminary x-ray data which shows that the tellurium lies in a

TABLE II

Compounds of Tellurium with Thiourea and Related Derivatives

Type	L=tu X=	L=etu X=	L=tmtu X=	L=prtu X=
$Te^{II}L_4X_2$	Cl*, Br, F*, SCN, NO$_3$, ClO$_4$, HF$_2$	Cl*, Br*, ClO$_4$		Cl, ClO$_4$
$Te^{II}L_2X_2$-cis	Br, Cl, I, SCN			Cl, Br
$Te^{II}L_2X_2$-trans	S$_2$O$_2$CH$_3$	Br, I, SCN, SeCN, S$_2$O$_2$CH$_3$	Cl, Br, I	
$Te^{IV}L_2X_4$			Br, Cl	
$Te^{II}L_3X_2$	F	ClO$_4$		ClO$_4$

*exists in anhydrous and dihydrate forms

tu = thiourea = $SC(NH_2)_2$

etu = ethylenethiourea = $SCN_2C_2H_4$

tmtu = tetramethylthiourea = $SC[N(CH_3)_2]_2$

prtu = propylenethiourea = $SCN_2C_3H_6$

centre of symmetry has also been obtained on almost all of the other known compounds of this type and it is thus assumed that they all possess TeL_4^{2+} cation type structures.

(b) $Te^{II}L_2X_2$ - cis

Structure determinations have been carried out on the $Te(tu)_2Br_2$ and $Te(tu)_2Cl_2$ compounds.[43] It is found that the TeS_2Cl_2 and TeS_2Br_2 groups are almost, but not exactly, planar with the angle between the TeS_2 and TeX_2 planes being about 11.5°. A slight distortion is also noted with respect to the bond angles at the tellurium, which deviate from 90° by about 3°. The Te-S bonds in these compounds are found to be relatively short at 2.47 and 2.48 ±0.1Å, while the Te-X bonds are relatively long at 2.92 and 3.05 ±0.1Å for the chloride and bromide respectively. Preliminary x-ray data for the $Te(tu)_2I_2$,[44] $Te(prtu)_2Cl_2$ and $Te(prtu)_2Br_2$[45] compounds indicate that the tellurium atom lies on a twofold axis and thus these compounds are proposed to be cis isomers as well.

(c) $Te^{II}L_2X_2$ - trans

$Te(etu)_2Br_2$ and $Te(etu)_2I_2$ have been shown to be trans, square planar in structure, with Te-S bond distances of 2.69 ±0.1Å in both cases, and Te-X distances of 2.78 and 2.97 ±0.1Å in the bromide and iodide respectively. The S-Te-Br and S-Te-I angles are 89.2 ±0.4°.[46] The structures have also been determined for $Te(tu)_2(S_2O_2CH_3)_2$,[47] $Te(etu)_2(S_2O_2CH_3)_2$[40] and $Te(etu)_2(SCN)_2$,[48]

where all three compounds are found to form trans square planes
with Te-S bond lengths ranging from 2.66 to 2.68Å, and S-Te-S
angles of 90° in all cases. Again the assumption that the other
compounds mentioned in this group are trans is based on preliminary
x-ray data,[40,49]which indicate that the tellurium atom lies in a
crystallographic centre of symmetry.

(d) $Te^{IV}L_2X_4$

In $Te(tmtu)_2Cl_4$ and $Te(tmtu)_2Br_4$[50]the tellurium atom
lies in a slightly distorted trans octahedron with Te-S bond
lengths of 2.70 and 2.69 ±0.1Å and Te-X bond lengths of 2.70 and
2.53 ±0.1Å in the bromide and chloride respectively. The Cl-Te-Cl
and Br-Te-Br bond angles are all 90° within the error, but a slight
distortion of the octahedron is noted in one of the X-Te-S angles
which is 98.7° in both compounds.

(e) $Te^{II}L_3X_2$

$Te(tu)_3(HF_2)_2$[51]exists as a dimeric $[Te(tu)_3]_2^{4+}$
cation and four $(HF_2)^-$ anions as shown in Figure 7. No assignments
as to the structure of the prtu analogs has been made.

(f) 3 Co-ordinate complexes

A number of complexes where the central tellurium is
essentially three co-ordinate have been studied, and include
$TeC_6H_5(tu)_2Cl$, TeC_6H_5tuCl, $TeC_6H_5(tu)_2Br$, $TeC_6H_5(tu)Br$ and
$TetmtuCl_2$.

The crystal structure determinations that have been

performed[52,53] on $Te(C_6H_5)tuCl$, $Te(C_6H_5)tuBr$ and $Te(C_6H_5)(tu)_2Cl$

show the formation of a square plane with one "vacant" position.

In this fourth position, trans to the phenyl, a bridging halogen

is observed with a Te-X contact much greater than the sum of the

covalent radii involved. A similar structure with a vacant position

trans to the tmtu group is proposed for $TetmtuCl_2$ from preliminary

x-ray data.[54]

2. Tellurium Di-Methyl Di-Iodide

The compound $TeMe_2I_2$ is found to exist in two forms,

first postulated[55] as cis and trans isomers, but later identified[56]

as a covalent and an ionic form. The x-ray crystal structure

determination has now been done on both these forms.[57,58] The

ionic form is found to consist of trigonal pyramidal Me_3Te^+

cations and square pyramidal $MeTeI_4^-$ anions where the ions are

bridged by four weak Te - I interactions which complete a distorted

octahedral environment around each tellurium atom. The covalent

form also has a tendency to achieve octahedral co-ordination

about the tellurium with two Te-C contacts two short Te-I contacts

and two long Te-I contacts.

3. Tellurium Dithiocarbamate Compounds

A number of related dithiocarbamate tellurium compounds

have been synthesized.[59,60,61] These compounds have a central

tellurium atom bonded to either four (in TeL_2) or six (in TeL_4)

sulphur atoms. (where L = diethyldithio-carbamate [dtc] and

morphyldithiocarbamate.)

The x-ray crystal structures of tellurium dimorphyl-dithiocarbamate and tellurium diethyldithiocarbamate have been determined[62,63] and they both show the tellurium atom to be surrounded by an irregular square plane of sulphur atoms with two pairs of trans long and short Te-S bonds of approximately 2.86 and 2.53 Å respectively. Unlike the thiourea complexes the bond angles in this compound deviate significantly from 90° with S-Te-S angles varying from 67° to 146°. The possiblility of the bonding orbitals of the central tellurium being s hybridized has been mentioned[62,63] as a possible explanation for the deviation of the bond angles from 90°.

The compound Te(L)$_4$ has been proposed from infra red and nuclear magnetic resonance data[61,62] to possess the structure as shown in Figure 8, with two unidentate and two mono-dentate ligands.
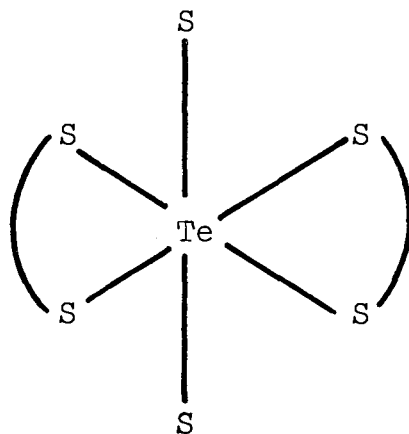
Figure 8.

Proposed Structure of Te(dtc)$_4$

II.   EXPERIMENTAL

A. The Mössbauer Spectrometer

The Mössbauer experiments were carried out on an Nuclear Science and Engineering Corporation (NSEC) AM-1 drive system and cryoflask, used in conjunction with a Nuclear Data 2200 series 1024-channel analyser as shown in Figure 9. The constant acceleration transducer was driven by a voltage pulse generated from the output of the scalar address of the multi-channel analyser. This synchronized the movement of the transducer with the multi-scaler of the analyser resulting in excellent linearity and reproducibility of the velocity drive. Using this spectrometer 2x256 channel sets of mirror image spectra were obtained with the transducer operating at 25 cycles per second and a dwell time of 80 microseconds per channel.

The cryoflask used with this system was a metal vacuum cryostat which held liquid nitrogen for c.a. 35 hours, maintaining source and absorber at 80°K. The cryoflask also held liquid helium for c.a. 12 hours.

The Mössbauer source and absorber compounds were mixed with a small amount of copper or silicon grease before being placed in the source or absorber holders. This was done firstly to give good thermal contact between the compound and the holder and secondly to even distribute the material over the holder ensuring uniform thickness.

A teflon absorber holder with o-ring seal was used to hold the absorber compounds studied.
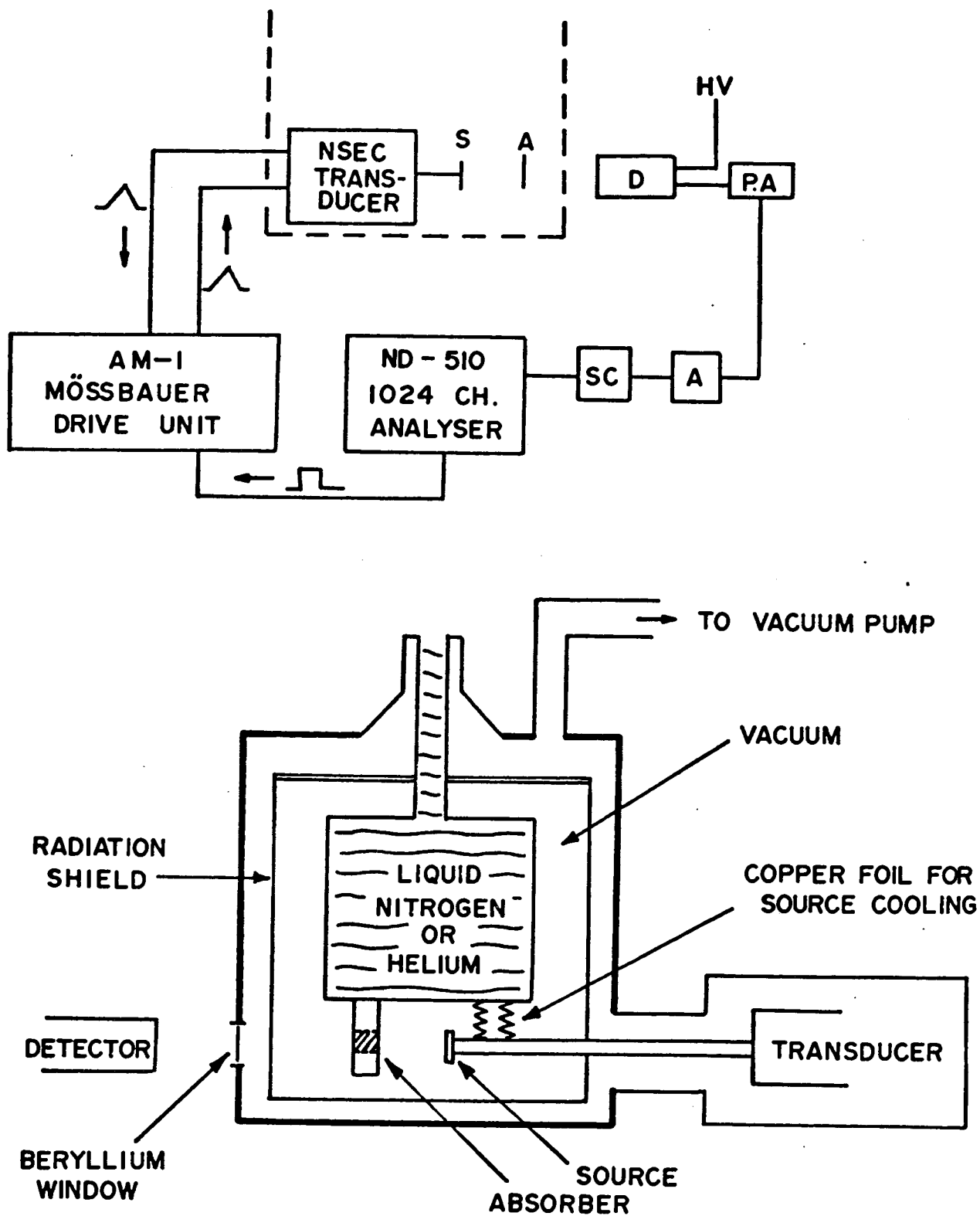
Figure 9.

Diagram of the Mössbauer Spectrometer

B. ^{125}Te Mössbauer

1. Sample Preparation

The compounds studied by ^{125}Te absorption Mössbauer were synthesized on a 20-100 mg. scale in high yields using 75% enriched ^{125}Te obtained from Oak Ridge National Laboratories. Elemental analyses were carried out on non-enriched sample preparations. Raman spectra were taken on both the non-enriched and enriched samples except in the case of the very darkly coloured Te(tmtu)$_2$Br$_4$ and Te(tmtu)$_2$Cl$_4$ compounds, for which Raman spectra could not be obtained. The results of the elemental analyses are shown in Table III. The preparations, which will be briefly described, have all been previously carried out on the 1 to 100 gm. scale.

The cis-Te(tu)$_2$Br$_2$, and cis-Te(tu)$_2$Cl$_2$[44] compounds were prepared by the reaction of four moles of thiourea with TeO$_2$ in the appropriate halo acid. The Te(tu)$_2$I$_2$[44], Te(tu)$_4$Br$_2$ and Te(tu)$_4$(SCN)$_2$[64] compounds were than prepared by the addition of NaI, KBr and KSCN respectively to an aqueous solution of Te(tu)$_2$Br$_2$ in the presence of excess thiourea. The Te(tu)$_4$Cl$_2$ compound was prepared by adding excess thiourea to a solution of Te(tu)$_2$Cl$_2$[64] in hot MeOH and Te(tu)$_4$(NO$_3$)$_2$[64] was then prepared by the addition of KNO$_3$ to an aqueous solution of Te(tu)$_4$Cl$_2$. Te(etu)$_4$Cl$_2$[66] was prepared by the additon of ethylenethiourea

TABLE III

Analytical Data

	C_f [a]	$C_{calc.}$	N_f [a]	$N_{calc.}$	Te_f [b]	$Te_{calc.}$
$Te(tu)_4Cl_2$	8.92	9.54	20.78	22.26	25.18	25.36
$Te(etu)_4Cl_2$	22.68	22.34	18.49	17.36	20.75	19.84
$Te(tu)_4Br_2$	8.28	8.11	19.29	18.39	21.51	21.56
$Te(tu)_4(SCN)_2$	13.07	12.84	25.74	25.55	23.06	23.27
$Te(tu)_4(NO_3)_2$	8.36	8.64	25.52	25.18	22.73	22.95
$Te(tu)_3(HF_2)_2$	8.38	8.31	19.71	19.40		
$Te(tu)_2Cl_2$	7.26	6.85	16.14	16.00	36.12	36.36
$Te(tu)_2Br_2$	5.38	5.47	12.58	12.76	29.29	29.01
$Te(tu)_2I_2$	4.61	4.50	10.65	10.51	23.63	23.91
$Te(etu)_2Br_2$	13.62	14.64	11.04	11.38	26.13	25.95
$Te(etu)_2I_2$	12.45	12.30	9.77	9.56	22.04	21.80
$Te(tmtu)_2Cl_4$	23.20	22.47	10.55	10.50	23.73	23.90
$Te(dtc)_4$	31.71	33.38	7.37	7.82		
$TeMe_2I_2$					30.70	31.00
$Te(tmtu)_2Br_4$	impure					
$Te(tmtu)Cl_2$	impure					

a) C and N analysese were carried out in this laboratory using a Perking Elmer 240, C, H and N Analyser.

b) Te analyses were carried out by Bernhardt Microanalytisches Laboratorium.

to TeO_2 in HCl and $Te(etu)_2Br_2$[65]was prepared by the addition

of a 4:1 mole ratio of etu to TeO_2 in 48% HBr while $Te(etu)_4Br_2$[66]

was prepared by the addition of an 8:1 etu:TeO_2 mole ratio, also

in 48% HBr. The trans iodide compound $Te(etu)_2I_2$[65]was then

formed by the addition of NaI to an aqueous solution of

$Te(etu)_4Cl_2$. The $Te(tu)_3(HF_2)_2$[67]compound was prepared by the

addition of an excess of thiourea to TeO_2 in HF. $Te(tmtu)_2Br_4$

and $Te(tmtu)_2Cl_4$[68]were both prepared by the addition of

tetramethylthiourea to TeO_2 in HBr and HCl repectively.

$Te(tmtu)Cl_2$[54]was then prepared by the addition of two moles

of tmtu to TeO_2 in HCl. The $Te(S_2CNEt_2)_4$ compound was not prepared

as reported but instead was prepared by the simple addition of a

large excess of sodium diethyldithiocarbamate to TeO_2 in HCl.

$TeMe_2I_2$ was prepared by heating Te metal and CH_3I in a sealed tube

at 80° for 48 hours.

The Raman spectra of these compounds were recorded on a

Cary 81 Laser Spectrometer and the infra red spectra were recorded

on a Perkin Elmer 457 spectrometer.

2. [125]Te Counting Techniques

In the [125]Te Mössbauer absorption experiments a 50

millicurie ^{125}I on copper source supplied by New England Nuclear

was used. In these experiments both the source and absorber were

cooled to 80°K. When using an ^{125}I source to populate the Mössbauer level difficulty arises in the detection of the 35.6 keV. Mössbauer gamma because of the high background of x-rays from the electron capture event and the highly internally converted Mössbauer transition itself. This leads to a very high tellurium x-ray background of 27.4 keV. and 31.2 keV. gammas which cannot be resolved from the Mössbauer gamma ray. To eliminate this a two atmosphere $Xe(CO_2)$ proportional detector was used. As Xe has a K absorption edge of 34.51 keV., whose energy then lies above the tellurium x-rays, only the 35.6 keV. gamma ray is capable of K-shell photo-electric absorption and subsequent excitation of Xe x-rays. The 6 keV. escape peak which then results from this photo-electric event is then counted in the Mössbauer experiment. A thin copper absorber is also placed directly in front of the source to reduce the background under the 6 keV. escape peak in the detector.

C. ^{129}I Absorption Mössbauer

1. Sample Preparation

The trans $Te(etu)_2{}^{129}I_2$ and cis $Te(tu)_2{}^{129}I_2$ compounds used in the ^{129}I absorption experiments were prepared in the manner described for the ^{125}Te samples only in this case ^{129}I obtained from the Oak Ridge National Laboratory as $Na^{129}I$ in aqueous solution was used.

2. ^{129}I Counting Techniques

The source used in the ^{129}I absorption experiments was a Zn^{129m}Te source prepared in the usual manner[69] using ^{129m}Te obtained by neutron irradiating ^{128}Te (>99%) metal at Chalk River Nuclear Laboratories.

The detecting system consisted of a Harshaw Na(Tl) x-ray detector, integrally mounted on a photo-multiplier tube, together with an Ortec model 113 preamplifier and model 440A selective filter amplifier. When using a ^{129m}Te source 27.47 keV. tellurium x-rays, which are irresolvable from the 27.7 keV. Mössbauer transition, are seen in all isomeric transitions feeding ^{129}Te and hence the background count in the experiment is very high. These ^{129}I experiments were also carried out at 80°K.

D. ^{129}I Emission Mössbauer

1.   Sample Preparation

These experiments were carried out with both ^{129m}Te and ^{129}Te as sources and were run with a Na^{129}I absorber. The ^{129m}Te source compounds were prepared in the same manner as that described for the respective ^{125}Te enriched compounds except that in this case ^{129m}Te labelled TeO$_2$ was used as a starting material The ^{129m}Te was obtained in the same way as described for Zn^{129m}Te. The experiments were carried out a 4°K. with the counting time thus being restricted to approximately twelve hours. (the maximum

time the dewar would hold liquid helium.)

A rapid radiochemical separation of ^{129}Te from ^{129m}Te[7]
for the preparation of the ^{129}Te(tu)$_2$Cl$_2$ compound was achieved
through the chemical effects of the isomeric transition in solution.
^{129m}Te-labelled telluric acid was dissolved in 4N HCl and in this
solution the ^{129m}Te → ^{129}Te isomeric transition produces bond
rupture in >90% of events giving ^{129}Te(IV) in solution. In the
presence of Te(IV) carrier, SO$_2$ is then bubbled through the
solution selectively reducing the ^{129}Te(IV) to tellurium metal, the
^{129m}Te remaining in solution as H$_6$^{129m}TeO$_6$. Using the 69 minute
^{129}Te labelled metal the preparation of ^{129}Te(tu)$_2$Cl$_2$ was then
rapidly carried out in the manner as described for the ^{125}Te
enriched sample, and its Mössbauer spectrum immediately recorded.

2. ^{129}I Absorber

The Na^{129}I absorber, used in the ^{129}I emission experiments
was prepared by the evaporation of an aqueous solution of Na^{129}I
obtained from Oak Ridge and contained ca. 15 mg. cm.$^{-2}$ of ^{129}I.
It was confirmed as a single line absorber against a Zn^{129m}Te
source and gave an isomer shift of -.50 ±.04 mm. sec.$^{-1}$ with a
line width of 1.09 ±.02 mm. at 80° K. At 4° K. a slightly broadened
line width of 1.24 ±.02 mm. was observed. The choice of sodium
iodide for an ^{129}I absorber was made because it possesses a large
recoil free fraction of f=0.29 and a high Debye temperature of
125° K. The same detecting system used in the ^{129}I absorption

experiments was used in the ^{129}I emission studies.

E.   Computer Analysis of Mössbauer Spectra

The Mössbauer spectra were fitted to Lorentzian absorption lines by means of a computer analysis. The program used required initial estimates of the line positions, full-widths, and intensities, and allowed for the constraining of any number of these parameters during the fitting procedure. In an ideal case, all such constraints should be removed during the latter part of the computation. However, for the more complex ^{129}I spectra, some of which contained two superimposed 8-line quadrupole split spectra, it was found necessary to constrain many of the absorption line parameters throughout the fitting process. The program gave a value of chi-squared, χ^2, for each fit, which allowed a ready assessment of the statistical acceptability of the fit. Only when the χ^2 value indicated a degree of confidence within the 5% and 95% limits, as determined by the number of degrees of freedom in the fit, was the computer fit of a spectrum judged to be acceptable.

All of the spectra obtained in this work were mirror-image spectra and the two halves were always computed separately.

III. RESULTS

A. ^{125}Te Mössbauer Data

The ^{125}Te Mössbauer parameters for the compounds investigated are given in Table IV and a number of sample spectra are shown in Figure 10. In Table V the values measured in the present work are compared with the literature values for those compounds which have previously been studied.

The values of the isomer shifts and quadrupole splittings quoted in Table IV are the mean values calculated from the two halves of the mirror image spectrum obtained, which were computed independently. The error bars thus quoted reflect the standard deviations generated by the computer fit and the errors between the two halves of the mirror image spectrum. Also, since the χ^2 values for the two halves of the spectrum were always in good agreement, the χ^2 value for the first half of each mirror image spectrum is quoted. The computed fits to the spectra were judged statistically acceptable (the 5% limit on χ^2 is 284 for 247 degrees of freedom) for all of the compounds except Te(tmtu)$_2$Br$_4$ and TetmtuCl$_2$ where the samples were expected[54,68] to contain small amounts of TetmtuBr$_2$ and Te(tmtu)$_2$Br$_4$ impurities respectively. The line width for the Te(tmtu)$_2$Cl$_4$ spectrum when computed as a single line was found to be significantly broader (9.5 mm. sec.$^{-1}$) than in the other spectra (6.5 - 7.9 mm. sec.$^{-1}$) and since the sample used was no thicker than in any other case it was assumed that the line broadening was due to a small quadrupole coupling.

TABLE IV

Mössbauer Parameters

	Compound[a]	$\delta^{(b,c)}$ mm. sec.$^{-1}$	$\Delta^{(c)}$ mm. sec.$^{-1}$	χ^2 for 247 degrees of freedom
1.	$Te^{II}(tu)_4Cl_2$	+0.93 ±.06	15.62 ±.06	286
2.	$Te^{II}(etu)_4Cl_2$	+0.93 ±.12	16.00 ±.21	289
3.	$Te^{II}(tu)_4Br_2$	+1.00 ±.06	15.65 ±.06	269
4.	$Te^{II}(tu)_4(SCN)_2$	+0.86 ±.07	16.11 ±.07	273
5.	$Te^{II}(tu)_4(NO_3)_2$	+0.87 ±.10	15.19 ±.18	285
6.	$Te^{II}(tu)_3(HF_2)_2$	+0.80 ±.06	15.55 ±.06	257
7.	$Te^{II}(tu)_2Cl_2$ Cis	+0.74 ±.06	15.22 ±.10	261
8.	$Te^{II}(tu)_2Br_2$ Cis	+0.74 ±.06	15.35 ±.07	263
9.	$Te^{II}(tu)_2I_2$ Cis	+0.80 ±.08	15.39 ±.12	261
10.	$Te^{II}(etu)_2Br_2$ trans	+1.00±.06	17.37 ±.04	281
11.	$Te^{II}(etu)_2I_2$ trans	+0.85 ±.08	16.16 ±.12	255
12.	$Te^{II}(tmtu)Cl_2$ trans	+0.58±.58	17.90 ±.12	318
13.	$Te^{IV}(tmtu)_2Cl_4$ trans 1 line	+1.60 ±.06	0	275
	2 lines	+1.58 ±.20	2.77 ±.32	272
14.	$Te^{IV}(tmtu)_2Br_4$ trans	+1.58 ±.07	0	361
15.	TeO_2	+0.91 ±.16	6.74 ±.2	224
16.	Te-METAL	+0.68 ±.08	7.16 ±.11	285
17.	ZnTe	-0.07 ±.08	0	264
18.	$Te(dtc)_4$	+1.3 ±.1	0	261
19.	$TeMe_2I_2$	+0.35 ±.17	7.3 ±.33	253

TABLE IV

a)   tu = Thiourea, etu = Ethylenethiourea, tmtu = Tetra-
     methylthiourea.

b) δ with respect to a ^{125}I on Copper source.

c) δ and Δ are the mean values computed from the two halves
     of the mirror image spectrum.

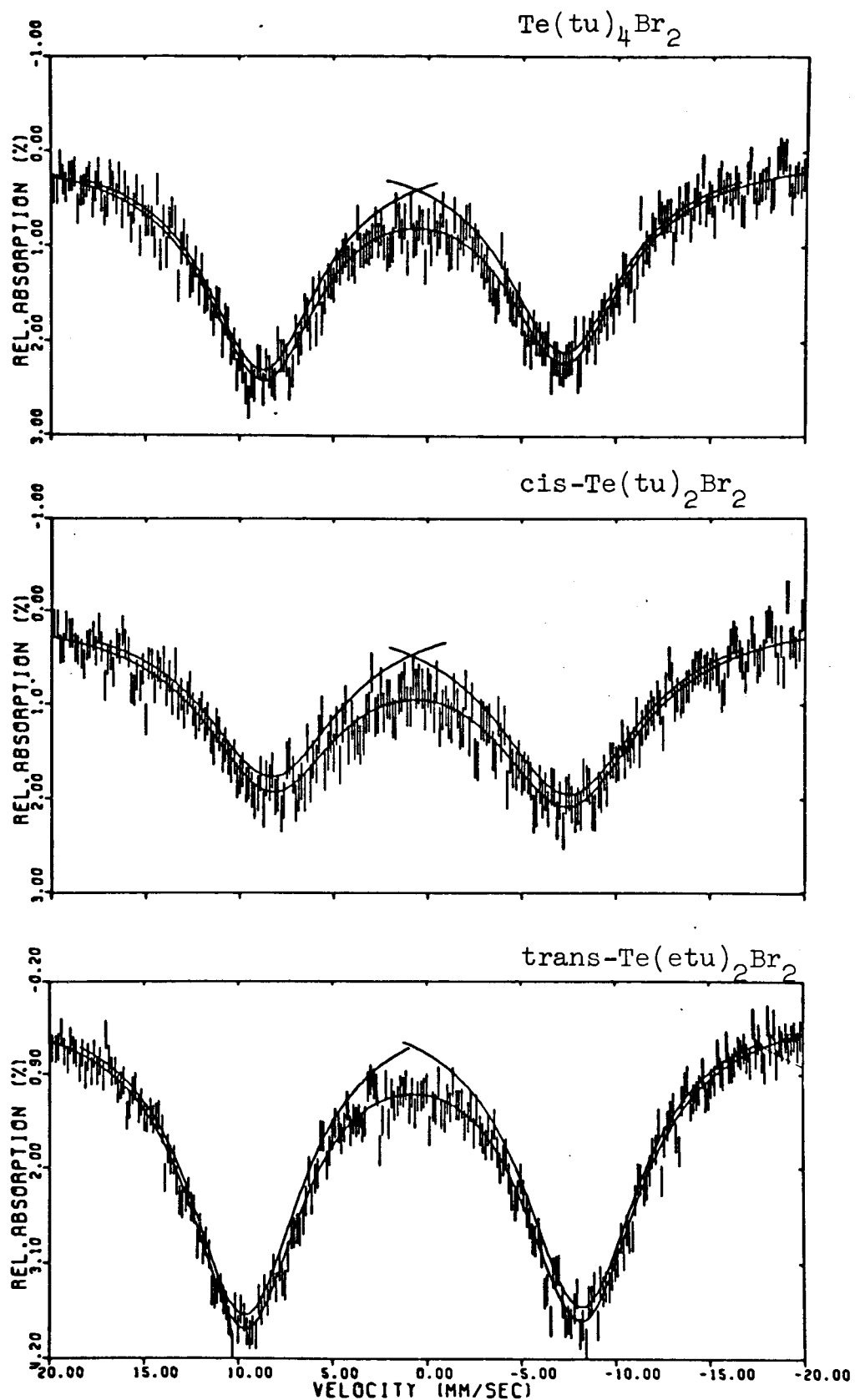d) χ^2 are again those for the first half of the mirror-
     image spectrum.

Figure 10. ^{125}Te Spectra of Te(tu)$_4$Br$_2$, cis-Te(tu)$_2$Br$_2$ and trans-Te(etu)$_2$Br$_2$

TABLE V

Comparison of Previously Reported ^{125}Te Mössbauer Data with that Obtained in the Present Work.

	* δ (mm. sec. $^{-1}$)	Δ (mm. sec. $^{-1}$)	REF.
Te METAL	+.50 ±.05	7.72 ±.11	7
	+.78 ±.10	7.10 ±.11	8
	+.51 ±.04	7.4 ±.2	11
	+.68 ±.08	7.16 ±.11	†
ZnTe	−.16 ±.04		8
	−.07 ±.08		†
TeO$_2$	+.74 ±.11	6.76 ±.09	7
	+.72 ±.02	6.63 ±.06	9
	+.84 ±.12	6.25 ±.03	5
	+.72 ±.07	6.54 ±.08	8
	+.73 ±.08	7.3 ±.1	10
	+.91 ±.16	6.74 ±.2	†
Te(SCN$_2$H$_4$)$_4$Cl$_2$	+1.49 ±.5	16.5 ±.8	1
	+.93 ±.06	15.62 ±.06	†
Te(SCN$_2$H$_4$)$_2$Cl$_2$	+1.49 ±.5	16.5 ±.8	1
	+.80 ±.08	15.39 ±.12	†

† present work

* δ are quoted in this table with respect to a ^{125}I on copper source.

When the spectrum was computed as two lines, as shown in Figure 11, an acceptable fit was obtained giving a quadrupole splitting of $2.77 \pm .32$ mm. sec.$^{-1}$ with equal line-widths of 7.3 mm. sec.$^{-1}$.

In Table VI the relative intensities of the two peaks in the quadrupole split spectra are shown for some compounds of interest.

B. Raman and Infra Red Spectral Data

The Raman data is given in Table VII along with that previously reported. The Raman spectra taken on enriched and non enriched samples were in all cases identical. The Infra Red data for some of the compounds is shown in Table VIII.

C. ^{129}I Absorption Mössbauer Data

The data obtained from the two ^{129}I absorption experiments that were carried out are shown in Table IX. Again, in this case the χ^2 values were within the 5% limit indicating that an statistically acceptable fit was obtained. As the spectrum for the cis $Te(tu)_2{}^{129}I_2$ compound was obtained at liquid helium temperatures while the trans $Te(etu)_2{}^{129}I_2$ spectrum was obtained at liquid nitrogen temperature a slight line broadening was found in the former case. The spectrum obtained for the trans $Te(etu)_2{}^{129}I_2$ compound is shown in Figure 12.

D. ^{129}I Emission Mössbauer Data

The Mössbauer parameters obtained in the ^{129}I emission spectra are shown in Table X and a number of sample spectra
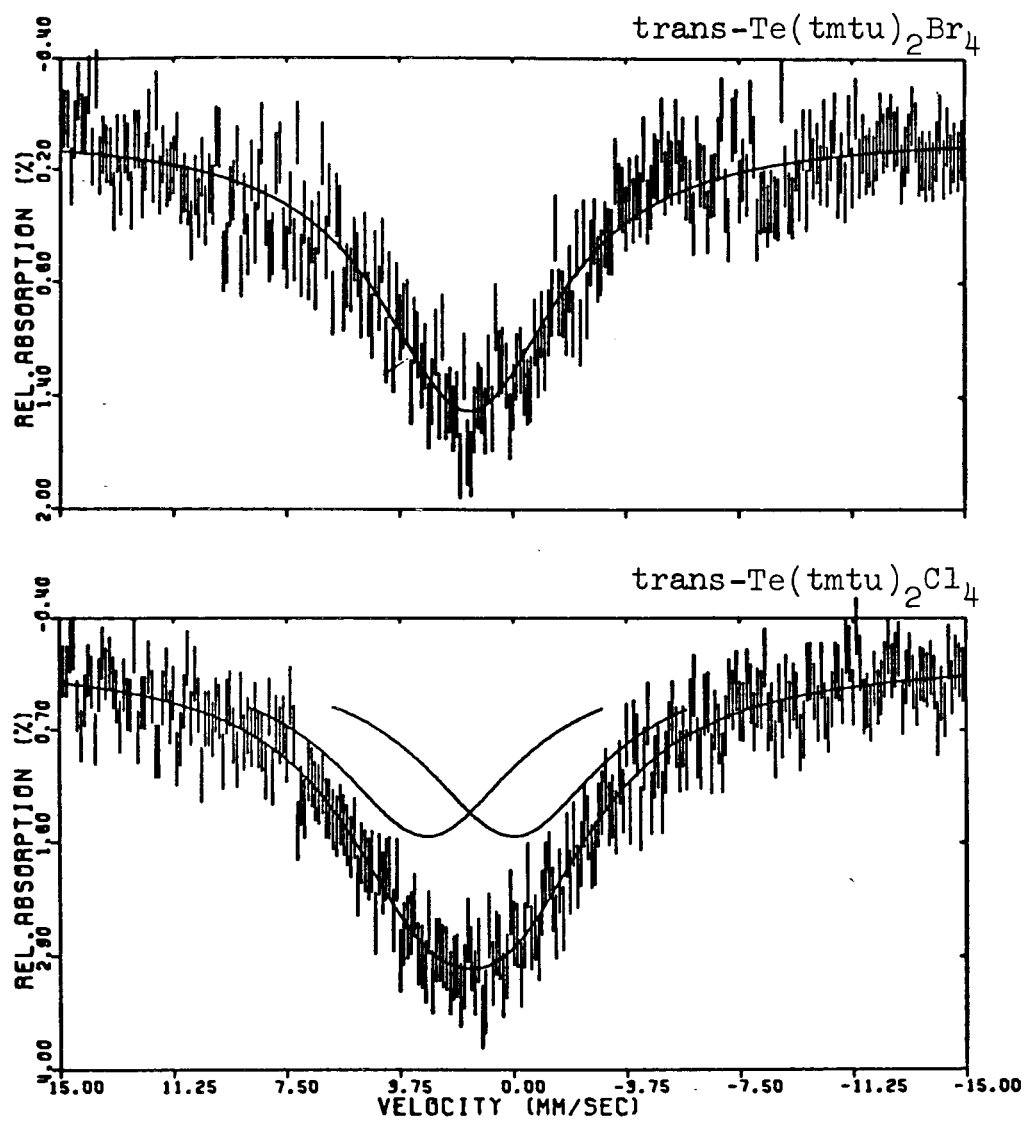
Figure 11.

^{125}Te Spectrum of Te(tmtu)$_2$Cl$_4$ and Te(tmtu)$_2$Br$_4$

TABLE VI

Relative Peak Intensities in the ^{125}Te Mössbauer Specta

Compound	% Intensity in Positive Velocity Peak	% Intensity in Negative Velocity Peak	Error in % Intensity
Te(tu)$_4$Br$_2$	53.2	46.8	2.5
Te(tu)$_4$Cl$_2$	53.3	46.7	2.3
Te(tu)$_4$(NO$_3$)$_2$	55.7	44.3	6.8
Te(tu)$_4$(SCN)$_2$	58.6	41.3	2.5
Te(tu)$_3$(HF$_2$)$_2$	51.1	48.8	2.2
Te(etu)$_4$Cl$_2$	55.7	44.2	2.6
Te(tu)$_2$Cl$_2$	52.2	47.7	3.5
Te(tu)$_2$Br$_2$	46.0	53.9	4.0
Te(tu)$_2$I$_2$	53.4	46.6	4.0
Te(etu)$_2$Br$_2$	50.0	50.0	1.3
Te(etu)$_2$I$_2$	50.8	49.3	3.9
Te(tmtu)Cl$_2$	56.9	43.1	3.3

TABLE VII

Raman Spectra

Compound	Found[a]	Reported[a]
1. $Te(tu)_4Cl_2$	234s 220sh 205m 120w 102m	[b] 235s 210sh 170w 104s
2. $Te(etu)_4Cl_2$	220s 191sh 182sh 140sh 93w	[c] 230sh 220sh 190s,br 184sh 157sh
3. $Te(tu)_4Br_2$	232s 205m 125w 113w 83m	
4. $Te(tu)_4(SCN)_2$	233s 138m 106w	
5. $Te(tu)_4(NO_3)_2$	240s 225sh 188w 169w 111m 79m	
6. $Te(tu)_3(HF_2)_2$	238s 219s 151w 127m 104m	
7. $Te(tu)_2Cl_2$-cis	278s 265m 192w 164w 127m 111m 87m 64m	[b] 278m 264m 247m 126m 111mw 84w
8. $Te(tu)_2Br_2$-cis	259s 255sh 186w 151w 115sh 100m 80m	[b] 261s 254m 184wm 120w
9. $Te(tu)_2I_2$-cis	233s 140m 108m 93m	[c] 233s 198w 178w 140m 109s 92m
10. $Te(etu)_2Br_2$-trans	208sh 190s br 143s 106m	[c] 227sh 212sh 190s,br 144sh 106m 94w 73m 49m
11. $Te(etu)_2I_2$-trans	183w 111s	[c] 233vw, 183w 111s 80w 44m
12. $Te(tmtu)_2Cl_4$	307w 246s 210s	
13. $Te(dtc)_4$	149s 307sh 330m 370s 430m	
14. $TeMe_2I_2$	149w 125sh 116s	

[a] Intensity designations are s strong, m medium, w weak, br broad, sh shoulder.

[b] P.J. Hendra, Z. Jovic; J. Chem. Soc. (A), 735, (1967)

[c] P.J. Hendra, Z. Jovic; Ibid.   911, (1968)

TABLE VIII

Infra-red Spectra

Compound	Found[a]
2. $Te(tu)_4Br_2$	3260s 3180s br 1610s, br 1390s, br 691m 590w 495 m,br
4. $Te(tu)_4(SCN)_2$	3265s 3120s 2040s 1978w 1610s 1385s,br 738w 695s 610m 480m 460m
5. $Te(tu)_4(NO_3)_2$	3360s 3280s 3160s 1620s 1360s, br 1065w 1050w 830w 898w 705s 550w 475w
7. $Te(tu)_2Cl_2$ Cis	3285s 3100s,br 1620s 1390s, br 680m 468m
8. $Te(tu)_2Br_2$ Cis	3275s 3080s,br 1610s,br 1390s,br 682m 468m 428m
9. $Te(tu)_2I_2$ Cis	3360s 3250s 3160s 1410s 1365m 700m 500m 462m

a) Intensity designations are:

s   strong   m   medium   w   weak   br   broad
sh shoulder

TABLE IX

^{129}I Absorption Mössbauer Data

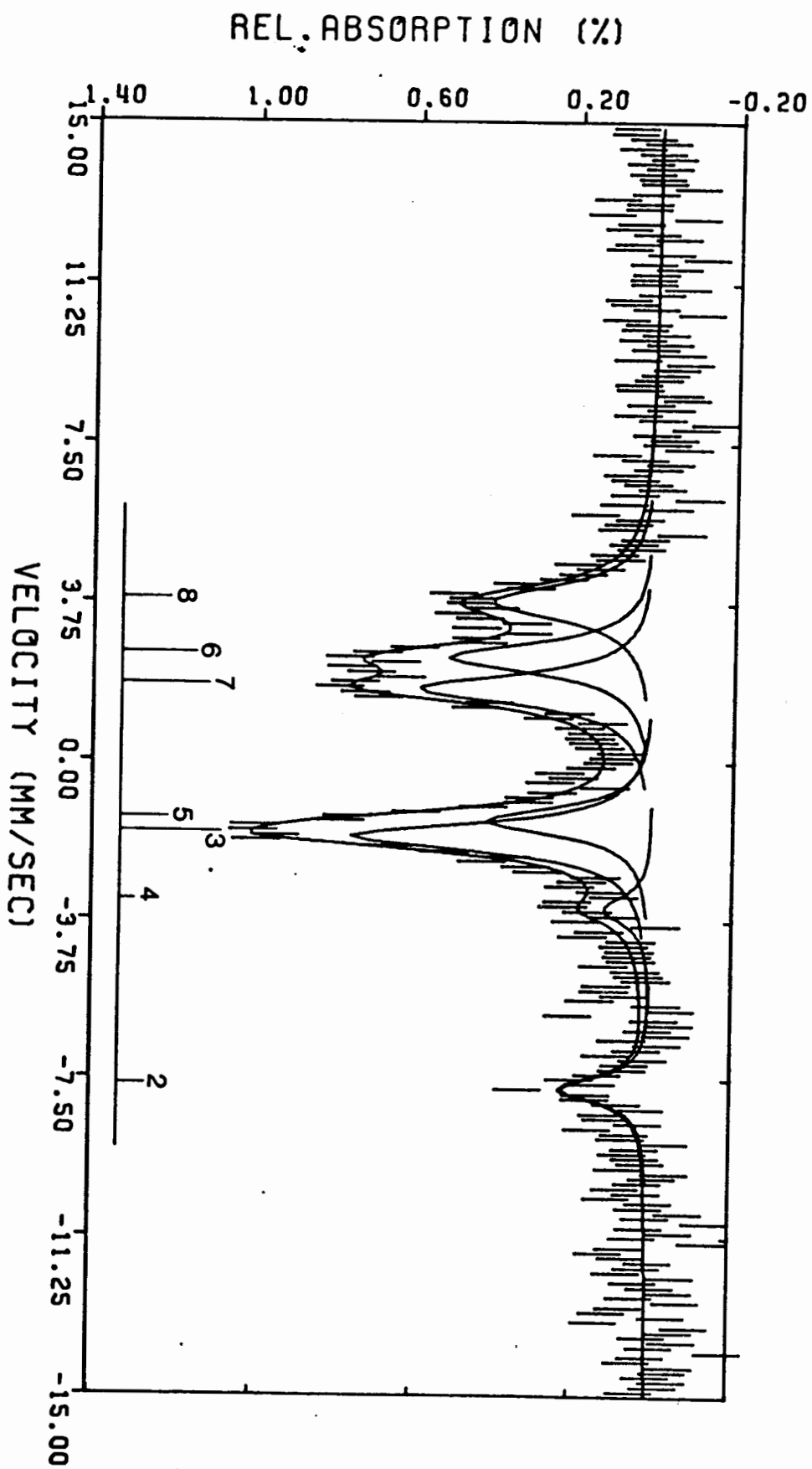|	$^{*}\delta$ mm. sec.$^{-1}$	e^2qQ Mc. sec.$^{-1}$	η
trans-Te(etu)$_2$^{129}I$_2$	+.010 ±.001	-597.7 ±6.2	0
cis-Te(tu)$_2$^{129}I$_2$	+.55 ±.06	-483 ±65	.45 ±.15

* measured with respect to a ZnTe source

Figure 12.

^{129}I Absorption Spectrum of trans-Te(etu)$_2$$^{129}I_2$

TABLE X

^{129}I Emission Mössbauer Parameters

Compound	*δ	e^2qQ	2Γ	χ^2
Labelled with ^{129m}Te	mm. sec.$^{-1}$	Mc. sec.$^{-1}$	mm. sec.$^{-1}$	
Te(tu)$_2$Cl$_2$	+0.99 ±.07 +1.14 ±.15	-1693 ±31 -1721 ±46	2.3 2.6	320 177
Te(tu)$_2$Br$_2$	+1.07 ±.08	-1704 ±35	2.8	268
Te(tmtu)$_2$Br$_4$	+1.04 ±.2	-1603 ±54	2.8	313
Te(etu)$_4$Br$_2$	+1.07 ±.2	-1645 ±66	3.4	267
Te(etu)$_2$Br$_2$	+1.06 ±.14	-1637 ±94	2.8	278
Te(tu)$_4$(SCN)$_2$	+0.99 ±.07	-1720 ±107	2.8	287
Compound Labelled with ^{129}Te				
^{129}Te(tu)$_2$Cl$_2$	+0.95 ±.3	-1685 ±173	2.0	264

* all parameters are converted to absorption parameters with δ being measured with respect to a ZnTe source.

are shown in Figure 13. Because of the very broad line widths obtained in the spectra some difficulty arose in obtaining statistically acceptable fits, and hence a number of the χ^2 values obtained were not within the 5% limit. However the excellent agreement between the Mössbauer parameters obtained for the different spectra indicated that further repetition of the experiments was not required and that the same, single, iodine species was formed in the radioactive decay in each case.
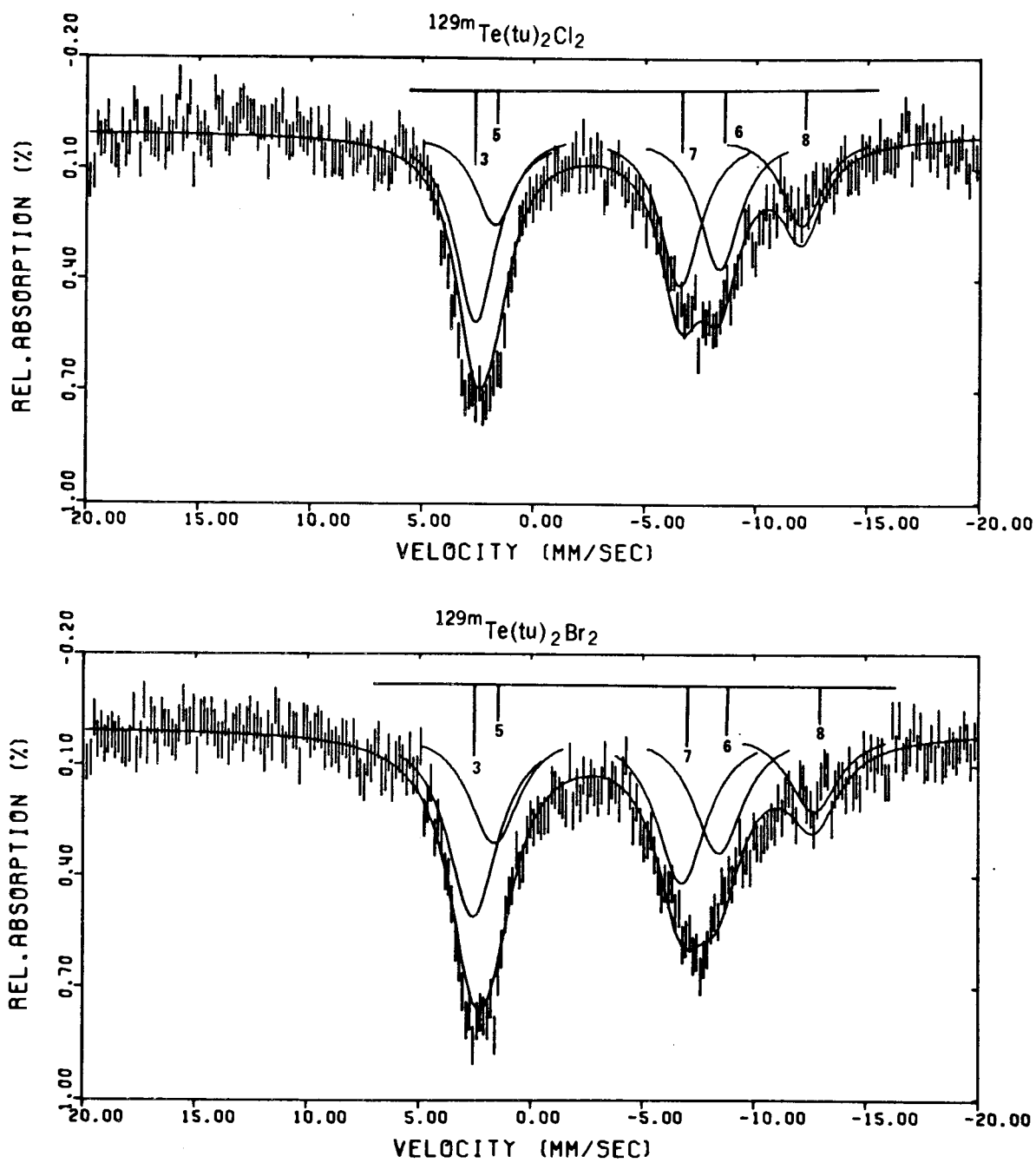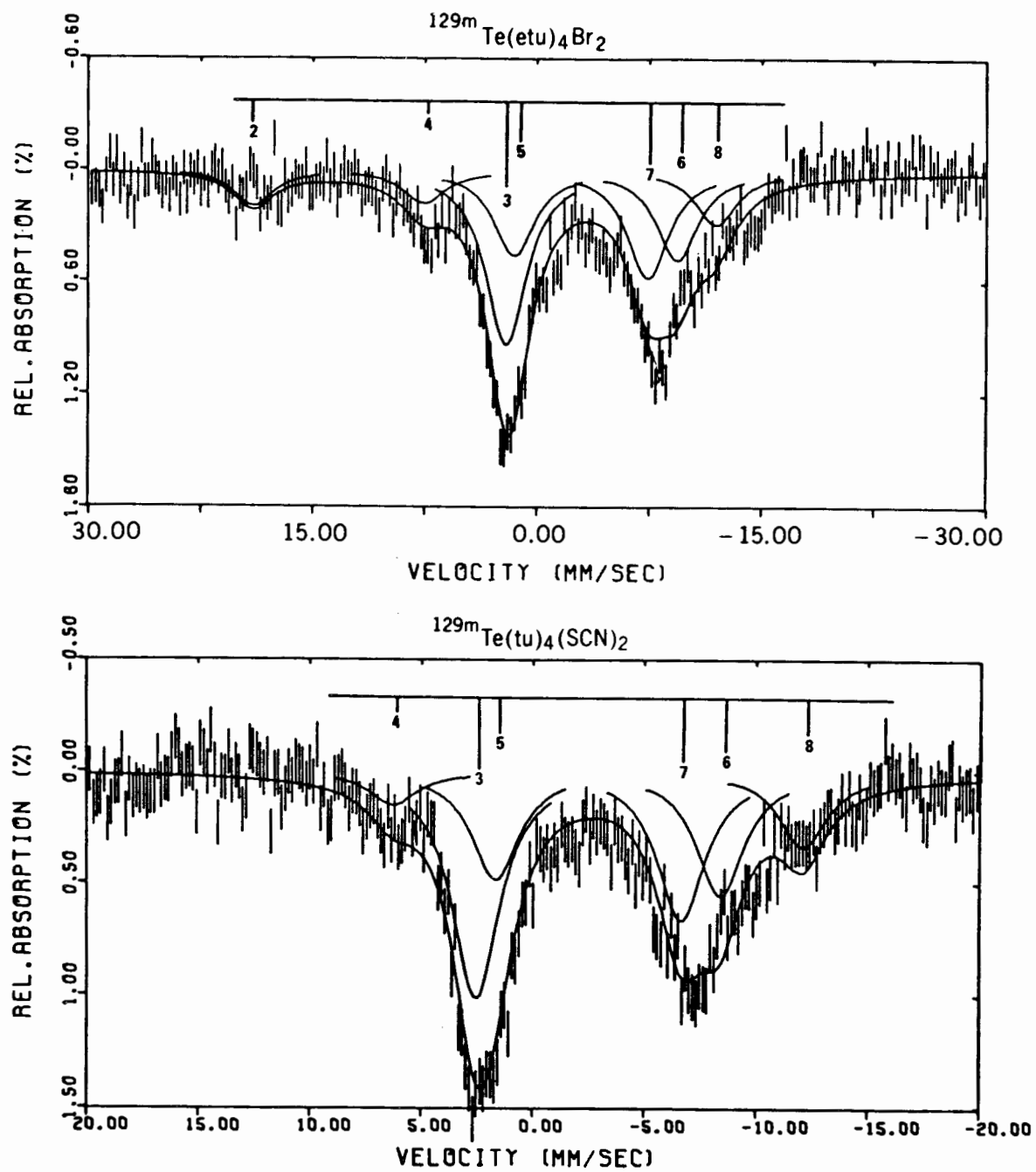
Figure 13. Sample ^{129}I Emission Spectra

Figure 13.   Sample ^{129}I Emission Spectra

IV DISCUSSION

A. Raman and Infrared Data

To aid in briefly discussing the structural implications of the Raman and Infrared data for the thiourea complexes, a summary of the Raman Te-S stretches, the Infrared C=S stretches and the calculated bond orders for some of the compounds are shown in Table XI. The bond orders were calculated using the formula[70]
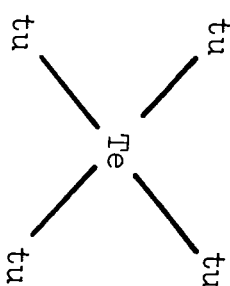
$$D_{(n)} - D_{(1)} = -.60 \log n \qquad (23)$$

where $D_{(n)}$ is the observed bond length, $D_{(1)}$ is the sum of the covalent radii and n is the bond order.

From Table XI it is apparent that in $Te(tu)_4X_2$ the C=S stretching frequency in the infrared was at 690-705cm.$^{-1}$, in cis-$Te(tu)_2X_2$ it was at 680cm.$^{-1}$ while in uncomplexed thiourea it is found at 730cm.$^{-1}$[71]. Thus a stronger C=S bond and a weaker Te-S bond is indicated for $Te(tu)_4X_2$ than for cis $Te(tu)_2Cl_2$ and $Te(tu)_2Br_2$. This is consistent with the structural data, which shows a Te-S bond length of 2.69 ±.01Å in $Te(tu)_4Cl_2$[41], which gives n=.34, and a Te-S bond length of 2.47 ±.01Å in $Te(tu)_2Cl_2$ and $Te(tu)_2Br_2$[43], which gives n=.97. The change in the C-S bond length in these two cases is unfortunately masked by the large error in the structure

TABLE XI

The Structures of the Tellurium-thiourea Compounds

	Te(tu)₄X₂ Square Planar	Cis-Te(tu)₂X₂ Square Planar with 2 short contacts and 2 long contacts	trans-Te(etu)₂X₂ Square Planar	trans-Te(tmtu)₂X₂ Octahedral
Te-S bond	$2.69\text{Å}(0.34)$, X=Cl [a]	$2.48\text{Å}(0.97)$, X=Cl[b] $2.47\text{Å}(0.97)$, X=Br[b]	$2.69\text{Å}(0.34)$[c], X=Br,I	$2.69\text{Å}(0.34)$, X=Cl[d] $2.70\text{Å}(0.34)$, X=Br[d]
Te-X bond		$2.92\text{Å}(0.12)$, X=Cl[b] $3.05\text{Å}(0.13)$, X=Br[b]	$2.78\text{Å}(0.36)$[c] X=Br $2.92\text{Å}(0.47)$, X=I	$2.52\text{Å}(0.54)$, X=Cl[d] $2.71\text{Å}(0.53)$, X=Br[d]
I.R. C=S stretch cm⁻¹	691, X=Br 695, X=SCN 705, X=NO₃	680, X=Cl 682, X=Br 700, X=I		
Raman Te-S stretch cm⁻¹	234, X=Cl 232, X=Br 233, X=SCN 240, X=NO₃	265, X=Cl 259, X=Br 233, X=I		

determination where C-S was found to be $1.75 \pm .06\overset{o}{A}$ in $Te(tu)_2Cl_2$, $1.76 \pm .05\overset{o}{A}$ in $Te(tu)_2Cl_2$ and $1.76 \pm .07\overset{o}{A}$ in $Te(tu)_2Br_2$.

The Raman data is also consistent with the trend in the calculated Te-S bond orders where the Te-S stretch is found at $232 - 240$ cm.$^{-1}$ for $Te(tu)_4X_2$, (X = Cl, Br, SCN, NO_3) and at 265 and 259 cm.$^{-1}$ for $Te(tu)_2Cl_2$ and $Te(tu)_2Br_2$ respectively.

In the cis-$Te(tu)_2I_2$ compound the spectral data, which shows the C=S stretch in the infrared at 700 cm.$^{-1}$ and the Te-S stretch in the Raman at 233 cm.$^{-1}$, indicates the formation of a weaker Te-S bond than in the corresponding choride and bromide compounds. This may be rationalized in terms of the change in electronegativity of the ligand, where the less electronegative ligand, I, would tend to form a more covalent Te-X bond. Making the assumption that the central tellurium uses only p orbitals in bonding to the ligands, this would have the effect of weakening the trans Te-S bond. Also, if we examine the Raman Te-I stretch for cis-$Te(tu)_2I_2$ (108 cm.$^{-1}$) we can see that it is almost identical to that found for trans-$Te(etu)_2I_2$ (106 cm^{-1}) where $Te(etu)_2I_2$ is found to contain a covalent Te-I bond with n = .47. Evidence for the dissimilarity between $Te(tu)_2I_2$ and $Te(tu)_2Cl_2$ (Br_2) is also noted below in the discussion of the Mössbauer parameters.

For the ethylenethiourea and tetramethylthiourea derivatives, the vibrational spectra were far more complex than for the thiourea derivatives and a discussion of the infrared and Raman data for these compounds lies out of the scope of this work.

B. ^{125}Te Mössbauer Spectra of the Tellurium Thiourea Compounds

1. Isomer Shifts

The results of Table IV show that for the $Te^{II}(tu)_4X_2$, cis-$Te^{II}(tu)_2X_2$ and trans-$Te^{II}(etu)_2X_2$ compounds the isomer shifts span a small range from .74 to 1.00 mm. sec.$^{-1}$ while in the $Te^{IV}(tmtu)_2X_4$ compounds the isomer shifts are ca. 1.60 mm. sec.$^{-1}$ Thus, there is a clear differentiation between the isomer shifts of the thiourea compounds with formal oxidation states of Te^{II} and Te^{IV}, the values being more positive for the higher oxidation state. This is as would be predicted if the tellurium uses pure p-orbitals in bonding in these compounds.

In this model for the square planar $Te^{II}(etu)_2X_2$, cis-$Te^{II}(tu)_2X_2$ and the trans-$Te^{II}(etu)_2X_2$ compounds the bonds may be considered to be formed through the 5px and 5py orbitals of the tellurium with the 5pz orbital directed out of the plane containing two non-bonding p electrons and the 5s orbital containing a stereochemically inactive lone pair. In the octahedral $Te^{IV}(tmtu)_2X_4$ compounds, where the tellurium is in a $5s^2 5p^0$ state the bonds will then be formed through the px py and pz orbitals. This increased loss of p electrons in going from Te^{II} to Te^{IV} would lead to increased de-shielding of the $5s^2$ electron lone pair from the nucleus, hence an increase in $|\Psi s(0)|^2$ at the nucleus and a commensurate positive increase in the isomer shift would be observed.

The $Te(tu)_4X_2$ compounds all have the same isomer shift within the error of the measurement, which indicates that the $Te(tu)_4^{2+}$ cation is present in each case as predicted by Foss[40] from preliminary x-ray data. Also $Te(etu)_4Cl_2$ has the same isomer shift as $Te(tu)_4Cl_2$ indicating that the etu and tu ligands play an identical role in bonding. Again this is consistent with the x-ray data which shows Te-S bond lengths of $2.69 \pm .01\overset{o}{A}$ in both compounds. The $trans\text{-}Te(etu)_2X_2$ compounds again have the same isomer shift as $Te(tu)_4Cl_2$ and thus there is no measurable effect on the isomer shift when two trans Te-X bonds (of bond order $\approx \frac{1}{2}$) are substituted for two Te-S bonds (of bond order $\approx \frac{1}{2}$).

In $cis\text{-}Te(tu)_2Cl_2$ and $Te(tu)_2Br_2$ however the isomer shifts are found to be slightly smaller than those for the $Te(tu)_4X_2$ compounds and this difference does appear to be statistically significant. In the cis compounds we have essentially the formation of a $Te(tu)_2^{2+}$ cation with two short Te-S bonds of bond order ≈ 1 trans to two X^- ions ($n \approx 1$). This asymmetry of bond orders must be caused by the marked difference in electronegativity between the sulphur and the bromine or chlorine atoms involved. It should be noted here that shortly after our ^{125}Te absorption experiments were completed the Mössbauer data for $Te(tu)_4Cl_2$ and $Te(tu)_2Cl_2$ were published by Aleksandrov et al.[1] but the large errors in his measurements ($\pm .5$ mm.sec.$^{-1}$) did not allow him to

detect any difference in the isomer shifts between these two compounds.

The isomer shift of cis-$Te(tu)_2I_2$ does not show the same trend as the corresponding chloride and bromide compounds. It in fact displays an isomer shift identical to that found for the trans- $Te(etu)_2I_2$ compound. This indicates that the bonding in cis-$Te(tu)_2I_2$, because of the decreased difference in the electronegativity between sulphur and iodine is now quite covalent, as in $Te(etu)_2I_2$, and the removal of similar p electron densities from the central tellurium occurs. This point is supported by the infrared and Raman data discussed earlier.

The isomer shift of $Te(tmtu)Cl_2$ is also found to be significantly lower than that of the other Te^{II} compounds and this point will be discussed along with quadrupole splitting for $Te(tmtu)Cl_2$ and cis-$Te(tu)_2X_2$ (X = Cl,Br) in a later section.

It is possible to discuss the above data more quantitatively. A relationship between the isomer shift and hp for ^{125}Te may be derived from the corresponding expression for ^{129}I and the ratio of $^{125}Te/_{129}{}_I$ isomer shifts.

$$\delta_{129_I} = 1.5\ hp - 0.54 \tag{9}$$

$$\frac{\delta_{(^{125}Te)}}{\delta_{(^{129}I)}} = +0.29 \pm .01 \tag{21}$$

Thus, since the shielding coefficients of p electrons on tellurium and iodine are equal, if we multiply Equation 9 by .29 ±.01 we will arrive at an expression which relates the isomer shift and hp for ^{125}Te.

$$\delta_{^{125}Te} = .44\ (\pm.02)hp - .23\ (\pm.07) \tag{23}$$

where δ is measured in mm. sec.$^{-1}$ with respect to an ^{125}I on copper source. This is within experimental error of the expression derived[9] from the Mössbauer and N.Q.R. data of the tellurium hexahalides. Equation 23 may then be used to calculate the p orbital populations for some of the above compounds. Five independent measurements of the isomer shift for the $Te(tu)_4^{2+}$ cation are available from the data of compounds 1-5 (Table IV) the average value of which is .90 ±.05 mm. sec.$^{-1}$. This gives a value of hp = 2.6 ±.2 and it then follows that the net charge on the Te in the $Te(tu)_4^{2+}$ cation is +.6 ±.2 and that the charge on each of the sulphurs is +.35 ±.07 as shown in Table XII. This charge of +.35 ±.07 for sulphur can then be used to calculate a net charge of -.7 ±.2 on each of the halogens in the trans-$Te(etu)_2X_2$ compounds.

2. Quadrupole Splittings

An examination of the quadrupole splittings in Table IV shows that for compounds 1-11 very large Δ values were obtained.

TABLE XII

Calculated Charge Distributions

Compound	hp	Charge on Tellurium	Charge on S	Charge on X
TeS_4^{2+}	2.6 ±.2	+0.6 ±.2	+.35 ±.07	−1.0
trans-$Te(etu)_2X_2$		+0.6 ±.2	+.35 ±.07	−.7 ±.2

This is consistent with the square planar structures of these compounds, where the unequal population of the pz orbital in comparison to the px and py orbitals gives rise to a large electrostatic field gradient at the nucleus.

In the $Te^{IV}(tmtu)_2X_4$ compounds where the Te is fully octahedrally co-ordinated a quadrupole splitting would be expected only if the Te-S and Te-X bonds have differing orbital populations. The fact that no quadrupole splitting is observed for $Te(tmtu)_2Br_4$ indicates that identical orbital populations are present on the tellurium atom in the Te-S and Te-Br bonds. The small but observable quadrupole splitting observed in $Te(tmtu)_2Cl_4$ then reflects the greater difference in the electronegativity between sulphur and the halogen in this compound.

If we now return to a discussion of the square planar complexes we can describe the quadrupole splittings obtained (e^2qQ_{mol}) by the following expressions, as described in the introduction:

$$e^2qQ_{mol} = -Upe^2qQ_{atom} \qquad (15)$$

$$Up = -Uz + \frac{Ux + Uy}{2} \qquad (16)$$

In a square planar complex $\eta = 0$, and then $\Delta = \frac{1}{2}|e^2qQ_{mol}|$. If e^2qQ_{atom} is known Up can then be calculated. Values for e^2qQ_{atom} for ^{125}Te have been calculated by Violet et al.[20] Shikazono[19]

and Pasternak and Bukshpan[21] from the ^{125}Te Mössbauer data of Te metal and TeO_2. The work of Violet et al. involved the calculation of Up (.82 ±.02) in tellurium metal and the assumption of a value of q_{atom}, the electrostatic field gradient which derives from one 5pz electron in tellurium, as calculated by Barnes and Smith[72]. They then computed q, the field gradient at the nucleus and thus having experimentally measured e^2qQ_{mol} were then able to calculate a value for Q, the nuclear quadrupole of the $+\frac{3}{2}$ excited state of ^{125}Te, $|Q|$ = .20 $^{+.03}_{-.02}$. Both Shikazono and Pasternak also assumed Barnes and Smith's value for q_{atom} and arrived at a value of Q ≈ .2 barns from TeO_2 Mössbauer data.

From our isomer shift analysis for the square planar TeS_4^{2+} cations hp = 2.57 ±.2 and since for a square plane hp=2Up then Up = 1.28 ±.1. If we average the Δ values of compounds 1-5 we then arrive at

$$|e^2qQ_{mol}| = 2\Delta = 31.4 \pm.3 \text{ mm. sec.}^{-1}$$
$$= 880 \pm 10 \text{ Mc. sec.}^{-1}$$

and thus it follows that

$$e^2qQ_{atom} \; ^{125}\text{Te} = 688 \pm 60 \text{ Mc. sec.}^{-1}$$

This value of e^2qQ_{atom} does not agree with that calculated by Violet et al.[20] (570 ±60 Mc. sec.$^{-1}$). This is not surprising

as the bonding in Te metal is not clearly defined and thus the numerical analysis of the orbital populations that they carried out would be extremely difficult. The same argument can be applied to Pasternak and Bukshpan's[21]calculation of Q and the agreement of their two calculations must be at least in part fortuitous.

e^2qQ_{atom} can now be used to calculate Up and thus test the assumption of pure p bonding in other compounds by comparison with hp calculated from their isomer shifts. If we now apply this analysis to cis-$Te(tu)_2Br_2$ and $Te(tu)_2Cl_2$ we have from the quadrupole splitting, Up = 1.3 ●.1, and from the isomer shift, hp_{av} = 2.20 ±.2, and since for a pure p bonded square plane hp must equal 2Up these compounds appear to show some slight deviation from pure p bonds. If we assume that this deviation is due to some s hybridization of the bonding orbitals on the tellurium an attempt can be made to estimate the extent of the s electron participation in the following way. Equation 10 for ^{129}I can be converted to ^{125}Te again by multiplying by the ratio $\delta_{125_{Te}}$. Then

$$\frac{\delta_{125_{Te}}}{\delta_{129_{I}}} = .29$$

$$\delta_{125_{Te}} = -2.7 \ (\pm.2) \ hs + .44 \ (\pm.2) \ hp - .23 \ (\pm.07). \qquad (24)$$

Assuming that hp = 2Up = 2.6 ±.2 this gives a value of hs = .1 ±.2. The very large error encountered here does shed considerable doubt on the numerical analysis in this case. However it is interesting

to note that the S-Te-S bond angles at the tellurium do deviate
from 90° by about 3°[43] in these cis compounds, consistent with
s-participation in the bonding.

The very large errors encountered in this analysis are
due to the inherently broad line widths found in the ^{125}Te Mössbauer
spectrum and hence the relatively large uncertainty in the
determination of the centroid of the lines. This uncertainty
could be reduced if the percent absorption in the observed spectra
was increased, This could be done by recording all the spectra
at 4° K. or by developing a source with a higher recoil free
fraction than the ^{125}I on copper source that was employed in this
study.

In Te(tmtu)Cl$_2$ we find a quadrupole splitting slightly
larger than in the other compounds but again an isomer shift
significantly lower than the range established for the other Te^{II}
compounds, indicating the participation of s orbitals in bonding.
In Te(tmtu)Cl$_2$ however the analysis of the bonding is complicated
by the fact that the compound is not a true square plane and an
asymmetry parameter η will effectively increase the magnitude of
quadrupole splitting. Thus hp cannot be deduced from Up and a
numerical estimation of hs is not possible.

C. ^{125}Te Mössbauer Spectra of Te(dtc)$_4$ and α- Tellurium Dimethyl
    Diiodide

1. Te(dtc)$_4$
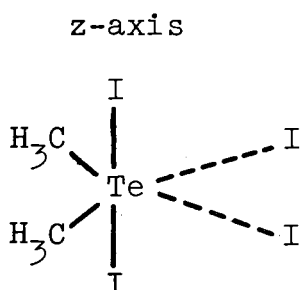
    In Te(dtc)$_4$ the tellurium atom is the formal oxidation

state of +4. However the isomer shift of this compound (+1.3 ±.1 mm. sec.$^{-1}$) is significantly lower than that found for the $Te^{IV}(tmtu)_2X_4$ compounds (1.58 ±.07 mm. sec.$^{-1}$) and this is indicative of s hybridized bonding orbitals on the tellurium. This conclusion is also supported by the fact that the S-Te-S bond angles of the bidentate ligands in the compound $Te(dtc)_2$, and hence in $Te(dtc)_4$, deviate significantly from 90°. The extent of this s hybridization can be estimated if we assume that hp in this compound is identical to that found in $Te(tmtu)_2Br_4$. This will give from Equation 24 hs = 1.0 ±.3. Thus in this case, where a large amount of s hybridization is involved, the numerical analysis of the Mössbauer data does produce a meaningful result.

2. α- Tellurium Dimethyl Diiodide

In α-tellurium dimethyl di-iodide the small quadrupole coupling is consistent with the known crystal structure, the tellurium being in a distorted octahedral environment. The low recoil-free fraction of this compound together with the small quadrupole coupling, leads to a very poorly resolved spectrum and large errors in the isomer shift and quadrupole splitting. As a result a quantitative interpretation of these parameters in terms of the population of the 5s and 5p orbitals on the tellurium was made very difficult. The very small isomer shift is consistent with either a small negative charge on the tellurium or the participation of some tellurium s-character in bonding. It is instructive to see whether the data can distinguish between these

two possibilities. A starting point in this analysis is to explain the quadrupole splitting. If we choose the I-Te-I axis as the z-axis then it is possible to determine Uz from ^{129}I absorption data for a similar trans I-Te-I configuration found in trans-Te(etu)$_2$I$_2$ (see ^{129}I absorption discussion).

z-axis

Then since Up =

$$\frac{e^2qQ_{mole}}{e^2qQ_{atom}} = .61 \pm .09$$

$$= -Uz + \frac{Ux + Uy}{2}$$

and if Ux = Uy . $= -Uz + Ux.$

Then if it is assumed that the charge on the iodines is $-.63 \pm .01$ as found in trans-Te(etu)$_2$I$_2$ then Uz = $.74 \pm .02$, Ux = $1.35 \pm .1$, and the charge on the tellurium will be $+.6 \pm .2$. This would predict an isomer shift of $.9 \pm .2$ mm. sec.$^{-1}$ which is not consistent with the observed value of $.35 \pm .17$ mm. sec.$^{-1}$ and does suggest that some s electron participation in the bonding orbitals on the tellurium atom is present. A meaningful numerical analysis of the extent of s hybridization however, cannot be carried out here

because of the large error in the isomer shift measurement.
If this analysis is carried a bit further the charges on the
methyl groups can be calculated as +.35 ±.1. It is found that
this charge state is not inconsistent with the proton nuclear
magnetic resonance data obtained (chemical shift = +3.3 ppm.
from T.M.S. ^{13}C coupling constant = 148 Hz.).

D.   The Goldanskii - Karyagin Effect

On examining the intensities of the two lines in the ^{125}Te Mossbauer spectra it was found that for a number of compounds one peak was signifantly more intense than the other as shown in Table VI.   Moreover it was noted that the more intense peak was always the peak which occurred at the more positive velocity in the spectrum (eg. $Te(tu)_4(Br)_2$ as shown in Figure 10).   As all the absorbers were ground into a fine powder and thus the single crystal effect would probably be ruled out it was concluded the cause of the asymmetry was the Goldanskii - Karyagin effect.

If we then examine the angular dependence of the transition probabilities (as calculated from Equation 8) in our square planar compounds we can see that for a polycrystalline

z-axis

$$\theta = 0, 180° \quad \frac{3}{2} \rightarrow \frac{1}{2} = 3$$

$$\frac{1}{2} \rightarrow \frac{1}{2} = 1$$

$$\theta = 90, 270° \quad \frac{3}{2} \rightarrow \frac{1}{2} = 3$$

$$\frac{1}{2} \rightarrow \frac{1}{2} = 5$$

sample, if it is assumed that the recoil free fraction for emission in the TeS_4 plane is greater than that for emission at 90° to the

plane, then it is possible to identify the more intense peak in the ^{125}Te spectrum as the $\frac{1}{2} \rightarrow \frac{1}{2}$ transition. Since this peak appears at a positive doppler velocity the ^{125}Te hyperfine splitting must be as shown in Figure 14.
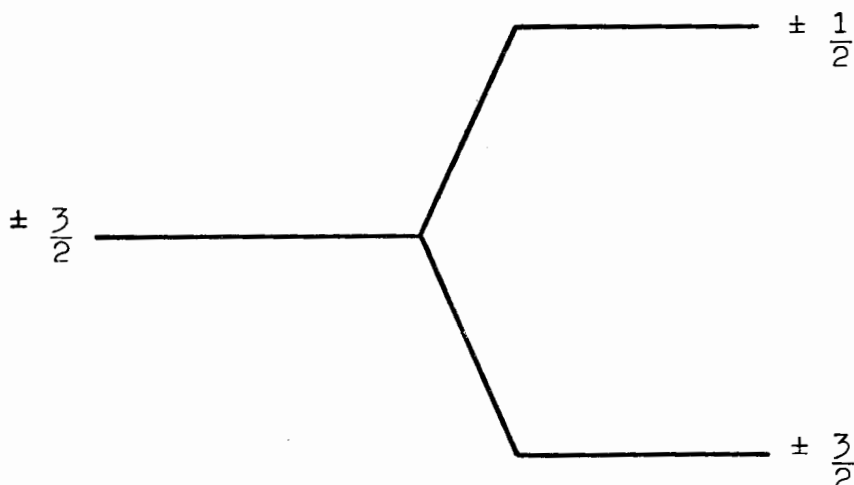

Figure 14.   Proposed Splitting of the ^{125}Te Mossbauer Level

Thus since q is negative for a square planar molecule, and the above splitting together with the expression

$$E_Q = \frac{e^2qQ}{4I(2I-1)} [3m_I^2 - I(I+1)] \qquad (5)$$
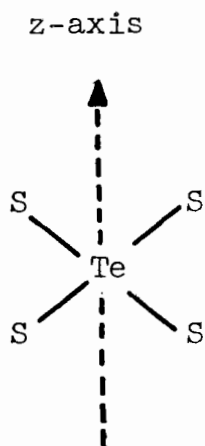
implies that e^2qQ is negative, then this means that Q ^{125}Te must be positive.

This is in direct disagreement with the negative sign
for Q calculated by Pasternak and Bukshpan.[21] Their calculation
involved the determination of the sign of the electrostatic field
gradient in TeO_2 from its [129]Te emission spectra. They stated
that the $\Delta m = 0$ transitions were enhanced (the ratio of peak 2
[$\Delta m = 0$] to peak 8 [$\Delta m = 1$] was changed from 6:10 to 7.5:10) thus
if a more intense peak was observed in the [125]Te spectra it could
then be identified as the $\frac{1}{2} \to \frac{1}{2}$ transition. No such effect however
was observed by Pasternak and Bukshpan and they had to refer to an
asymmetric spectrum reported by Stepanov et al.[73]. Stepanov
et al.'s spectrum of TeO_2 however was a very poor spectrum
consisting of four overlapping lines which they state resulted
from the presence of both rhombic and tetragonal TeO_2 and no
numerical intensity analysis of their data was performed. Thus
the evidence presented by Pasternak and Bukshpan was not sufficient
to conclude that Q [125]Te is in fact negative.

E. [129]I Absorption Mössbauer

To check the validity of the p-bonding model for the
tellurium compounds studied the [129]I Mössbauer absorption spectra
were measured on cis-Te(tu)$_2$[129]I$_2$ and trans-Te(etu)$_2$[129]I$_2$.
From the parameters obtained (shown in Table IX) for
trans-Te(etu)$_2$I$_2$ it was found that hp = Up = +.37 ±.01. This
indicates that the iodine is using pure p orbitals in forming a

bond with the central tellurium atom. This analysis predicts
that the effective charge on the iodine should be -.63 ±.01
which is in agreement with the value of -.7 ±.2 arrived at
from the ^{125}Te isomer shift data. Thus, within the very large
errors involved, the independent measurement of the ^{129}I isomer
shift in this compound leads to the same value of the effective
charge on the iodine as may be deduced from the ^{125}Te isomer
shift. This may be taken as evidence for the proposal that the
tellurium uses p-orbitals in bonding in this compound.

The preparation of cis-Te(tu)$_2$^{129}I$_2$ was not straight
forward and all attempts to synthesize this compound on a small
scale resulted in the production of a very small yield of the
red-coloured cis iodide together with some yellow cis bromide
impurity. Two sample preparations of this compound, however,
yielded the same ^{129}I Mössbauer parameters and thus we are
reasonably confident that the data is reliable even though
no identification of the compound by Raman or elemental analyses
was possible.

The data obtained supports the proposal that was
made earlier in the discussion of the Raman, infrared and ^{125}Te
Mössbauer data, that a covalently bonded iodine is present in
cis-Te(tu)$_2$I$_2$ rather than an I$^-$ ion. If we carry out an hp and
Up analysis of the data, however, it is found that, unlike trans-
Te(etu)$_2$I$_2$, the iodine in cis-Te(tu)$_2$I$_2$, is not bonding simply
through an iodine 5p orbital (Up = .30 ±.06, hp = .71 ±.08).

Moreover a very large asymmetry parameter (η = .45 ±.16) is present. This would indicate that some donation from the 5px and 5py orbitals on the iodine to, presumably, the 5d orbitals on the tellurium is occuring. The fact that this does not occur in trans-Te(etu)$_2$I$_2$ may be a direct result of the trans configuration of the two iodines.

In order to interpret the apparent π-bonding more quantitatively a more accurate measurement of η would be required. This will require further measurements on Te(tu)$_2$^{129}I$_2$ possibly using a Zn^{129}Te source rather than a Zn^{129m}Te source to give larger percent effects.

F. ^{129}I Emission Mössbauer

1. Comparison with Predicted Results

As the $\dfrac{^{125}\text{Te}}{^{129}\text{I}}$ isomer shift and quadrupole splitting ratios

for isoelectronic and isostructrural environments have been determined from previous ^{129}I emission studies, it is possible to predict the ^{129}I Mössbauer parameters which should be obtained in an ^{129}I emission experiment, if the molecule under study remains intact following the decay. The values predicted from the ^{125}Te absorption data (Table IV) are listed in Table XIII for the compounds which were studied.

From Table IX however it can be seen that all the emission experiments yielded the same Mössbauer spectra which showed a

TABLE XIII

^{129}I Mössbauer Parameters as Predicted

from ^{125}Te Mössbauer Parameters

Compound	* δ mm. sec.$^{-1}$	Δ Mc. sec.$^{-1}$
Te(tu)$_2$Br$_2$	+2.79 ±.3	+1959 ±60
Te(tu)$_4$Br$_2$	+3.45 ±.3	+1993 ±60
Te(etu)$_4$Br$_2$	+3.45 ±.3	+2042 ±65
Te(etu)$_2$Br$_2$	+3.69 ±.3	+2217 ±65
Te(tmtu)$_2$Br$_4$	+5.69 ±.3	0
Te(tu)$_2$Cl$_2$	+2.79 ±.3	+1942 ±60

* measured with respect to ZnTe source in an absorption experiment

single iodine species with an average isomer shift of 1.04 ±.02 mm. sec.$^{-1}$ and an average quadrupole splitting of 1667 ±27 Mc. sec.$^{-1}$. As these parameters do not correspond to any of the predicted values in Table XIII it may be concluded that molecular disruption occurred following the decay of ^{129m}Te in all the compounds studied. Also, since the emission spectra of ^{129}Te labelled Te(tu)$_2$Cl$_2$ yielded the same spectrum as the ^{129m}Te labelled samples it is concluded that this disruption was due to the instability of the daughter species rather than being a direct consequence of the radioactive decay.

2.   Proposed Identification of the Observed Species

If we examine the Mössbauer parameters of the iodine species formed in the radioactive decay, it is found that the sign of the quadrupole splitting is negative, thus indicating a linear bond. In the case of a linear bond, if only p orbitals on the iodine are used in bonding, then as discussed previously hp should be equal to Up. From the emission experiments we have:

$\delta = 1.50$ hp $- .54$ $e^2qQ_{mol} = 1667 \pm 27$ Mc. sec.$^{-1}$

$\delta = 1.04 \pm .02$ mm. sec.$^{-1}$ $e^2qQ_{atom} = 1607$ Mc. sec.$^{-1}$

hp $= 1.06 \pm .03$ Up $= 1.04 \pm .02$

Thus we can see that within the errors involved hp = Up and it may be concluded that the iodine species observed is using only p orbitals in bonding.

There are a number of possible linear fragments which could be formed following the decay such as I-S(tu, etu or tmtu), S-I-S, I-X, S-I-X or X-I-X, (X = halogen). However, if we consider that all the tellurium parent compounds gave the same iodine emission spectra;

a) when different halogens were present (as in $Te(tu)_2Cl_2$ and $Te(tu)_2Br_2$)

and

b) when no halogen was present (as in $Te(tu)_4(SCN)_2$), it would appear that the fragment formed was in fact a linear S-I-S or I-S fragment. Since it is most unlikely that cis-$Te(tu)_2X_2$ would rearrange on decay to give a linear S-Te-S fragment, it may be tentatively concluded that the species formed in the radioactive decay is, in all cases, simply the I-S (tu, etu, tmtu) molecule. The isomer shift and quadrupole coupling both indicate one p-hole on the iodine and that the iodine is present as I^0. This is not inconsistent with the electro-negativities of sulphur and iodine.

The Mössbauer emission experiment provides no direct evidence of the mechanism of the molecular dissociation or the chemical form of the non-iodine containing fragments produced. As mentioned above the fact that ^{129m}Te and ^{129}Te sources gave the same emission spectra points to the fact that the molecular decomposition occurs because of chemical instability rather than excitation caused by the radioactive decay. The environment of

the I-S molecule in the crystal is certainly an unusual one. The very low recoil free fraction observed must reflect the low binding energy of the molecule in the lattice. The very broad line widths may arise through a spectrum of isomer shifts and quadrupole splittings due to distortions in the lattice environment caused by surrounding molecular debris. Alternatively long and short-lived electronic states may be present which would give rise to a change in the effective half-life of the chemical state and would also produce line broadening.[74]

It is also interesting to note here that line 2 ($\Delta m = 0$) in the ^{129}I emission experiments is diminished in intensity to the point that in some of the spectra it was not observable. The poor quality of these spectra however did not allow any exact intensity measurements but this decrease in the intensity of line 2 is observed in all spectra. If it is assumed that in our emission spectra we are observing an I-S fragment, where the recoil free fraction will be enhanced with emission along the bonding axis, (z axis) we would expect a decrease in intensity of the $\Delta m = 0$ transitions. This effect should be observed for lines two, five and seven but as these latter two lines are broad overlapping lines no such observations were made in those cases. Though no accurate intensity calculations were possible and admittedly this evidence from the emission spectra is at the least very tenuous it is interesting to note that the observation of decreased intensity of line 2 is consistent with our proposal of the formation of a linear I-S fragment.

V SUMMARY

The ^{125}Te Mössbauer study carried out did serve to establish a range of isomer shifts and quadrupole splittings for Te^{II} square planar compounds. It also pointed out the inherent limititations of ^{125}Te Mössbauer when numerical analyses of s and p orbital populations are carried out.

The ^{129}I emission experiments were not successful in producing a large number of novel iodine compounds but did produce the formation of one unusual species.

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