

Interpretation of Unresolved Mössbauer Spectra in Compounds of I^{129} *

M. I. DA COSTA JR** , P. DA R ANDRADE[†] and P. J. VICCARO

Instituto de Física, Universidade Federal do Rio Grande do Sul^{††}, Pôrto Alegre RS

Recebido em 2 de Setembro de 1971

The I^{129} Mossbauer-effect absorption spectra of the rare earth tri-iodides, LaI_3 , GdI_3 and ErI_3 show **evidence** of unresolved quadrupole **splitting**. We propose that the **electric field gradient** (EFG) responsible for the interaction can be associated with a partially **filled** p hole (h_p) in the $5s^25p^6$ **electronic configuration** of I-. The quadrupole **coupling parameters** and **isomer shifts** are determined from a **least squares** fitting of the data using as initial estimates the Ci^{35} NQR data for **equivalent** rare earth *tri-chlorides*. For LaI_3 , GdI_3 and ErI_3 these are $e^2qQ = -80 \pm 8$ MHz, -115 ± 8 MHz, -144 ± 8 MHz; $\eta = 0.20, 0.50, 0.44$; $h = 0.18, 0.20, 0.21$; and $6 = -0.285 \pm 0.033$ mm/sec, -0.273 ± 0.033 mm/sec, -0.249 ± 0.033 mm/sec, respectively. The degree of **covalent bonding** in these compounds is discussed in terms of an overlapping orbital model.

Os espectros de absorção por Efeito Mossbauer do I^{129} nos tri-iodetos de terras raras, LaI_3 , GdI_3 , e ErI_3 mostram evidência de um desdobramento **quadrípolar** não-resolvido. Propõe-se que o gradiente de campo **elétrico** (EFG) responsável pela interação pode ser associado a um buraco p (h_p) parcialmente cheio na configuração eletrônica $5s^25p^6$ do I-. Os parâmetros do **aplamento quadrípolar** e os deslocamentos isomérius são determinados por um **ajuste** de mínimos quadrados dos dados, usando-se como estimativa inicial os dados obtidos por NQR do Ci^{35} nos *tricloretos* de terras raras equivalentes. Estes são, para o LaI_3 , GdI_3 e ErI_3 , respectivamente: $e^2qQ = -80 \pm 8$ MHz, -115 ± 8 MHz, -144 ± 8 MHz; $\eta = 0.20, 0.50, 0.44$; $h = 0.18, 0.20, 0.21$; e $6 = -0.285 \pm 0.033$ mm/s, -0.273 ± 0.033 mm/s, -0.249 ± 0.033 mm/s. O grau de ligação **covalente** nestes compostos é discutido em **têrmos** do **modelo** de superposição orbital.

1. Introduction

Recently, unresolved I^{129} Mossbauer spectra of the rare earth tri-iodide compounds LaI_3 , ErI_3 and GdI_3 have been reported¹.

*Work partially supported by CNPq (Brasil), BNDE (Brasil), CAPES (Brasil), CPq (UFRGS), CNEN (Brasil) and IAEA.

**Submitted in partial fulfillment of the requirements for the degree of Master of Science at Universidade Federal do Rio Grande do Sul.

[†]Senior Research Fellow, Conselho Nacional de Pesquisas (Brasil).

^{††}Postal Address: Rua Luiz Englert, s/n, 90000 - Pôrto Alegre RS.

It seemed **very** interesting to correlate these results with known Nuclear Quadrupole Resonance (NQR) measurements² of quadrupole interactions **in** similar tri-chloride compounds in order to **estimate** the quadrupole interactions expected for the tri-iodides. In this paper, we report these estimateú values obtaineú by a least squares fit to the experimental Mössbauer spectra with theoretical curves calculated using the estimated quadrupole interaction parameters. The interpretation of the electric field gradients derived and the departure of ionicity are **based** on the theory of covalent bonding described by Townes and Schawlow³ and the theory of overlapping orbitals, described by Owen and Thornley⁴.

2. Estimative of the Electric Field Gradients and the Quadrupole Interaction Parameters

It has been reported¹ that the I^{129} Mossbauer-effect spectra of the rare earth iodides, LaI_3 , GdI_3 and ErI_3 exhibit unsplit absorption resonances. However, the preliminary attempts to fit the resonances with single Lorentzian peaks resulted in questionable values for the isomer shift.

Recently, it was shown⁵ that the **presence** of unresolved quadrupole splitting can affect the determination of isomer shift values in cases where **the** Mossbauer transitions involve nuclear levels with spin larger than 3/2.

The reevaluation of the original I^{129} data indicates that this indeed may be the situation. In particular, the "singleline" resonance associated with each of the compounds exhibit a **definite** asymmetry. Furthermore, the relative **line** widths of the resonances cannot be correlated to thickness **broadening effects**. **Both** of these observations would be consistent with **the** idea of unresolved quadrupole splitting.

In fact, this possibility is quite reasonable, if one considers the Cl^{35} Nuclear Quadrupole Resonance (NQR) data² for **the** equivalent rare earth tri-chloride compounds. In this latter series, a non-zero quadrupole **coupling** was observed.

The **origin** of the electric field gradients (EFG) responsible for the quadrupole interaction is by **itself** an interesting point. In particular, if one assumes that the halide ions possess ionic **valence** of 1-, then the **electronic configuration** for both the I^- ($5s^2 5p^6$) and Cl^- ($3s^2 3p^6$) consist of closed shells **and** consequently cannot contribute to the EFG. This would imply that these gradients are associated entirely with the lattice electric field.

However, it was pointed out in the NQR study of the rare earth tri-chlorides that the observed quadrupole couplings can not in fact be explained by such purely "ionic" model. Moreover, monopole sum calculation⁶ for the rare earth tri-iodide compounds indicated that the quadrupole coupling constants associated with the lattice EFG are much smaller than the natural line width of I^{129} and therefore inconsistent with the broadening and asymmetry observed in the Mossbauer data.

One is led then to consider that departures from the purely ionic model could be responsible for the quadrupole couplings. For I^{129} , the consequences of such a departure become evident when one considers the relationship between the number of p holes, h , in the $5p$ electronic shell and the isomer shift. In particular, it has been shown⁷ that

$$\delta = 1.36 h_p - 0.54 \text{ (mm/sec)}, \quad (1)$$

where -0.54 mm/sec ($= \delta_0$) is the isomer shift of "ionic" I^- relative to a $ZnTe^{129}$.

From relation (1) and the "average" isomer shifts reported for the rare earth tri-iodides, we see that $h \neq 0$. Such departures from ionicity result in a partially occupied p-hole in the $5p$ electronic shell which could account for the EFG responsible for the observed quadrupole interaction.

These so-called covalent effects have been considered by Townes and Schawlow³. In particular if the ionic bond between the iodine and rare earth ligands has a fractional importance x in the structure and the pure covalent bond an importance $1-x$, then each contributes an amount to the EFG ($\propto eq$) given by the products of the fractional importance and the values of the EFG associated with each type of bond; i.e.,

$$eq_I = (1-x)eq_{510} + x(o) = (1-x)eq_{510}, \quad (2)$$

where, in the notation of Ref. 3, eq_{510} is the field gradient due to a $5p$ hole.

The quantity $(1-x)$ is called the amount of unbalanced p electrons (or holes), U_p , oriented along the bond. For any type of bond, the net effect of the valence p electrons may be expressed as the number of unbalanced p electrons, U_p , oriented along the bond. We then have that the quadrupole coupling constant is given by:

$$e^2 q_{mol} = U_p e^2 q_{at} Q, \quad (3)$$

where eq_{at} is the EFG due to the lowest p-hole state in the closed shell $5p^6$.

This implication that the EFG in the rare earth tri-halides may be associated with an unbalanced $5p$ hole allows us to estimate the quadrupole coupling constant in the rare earth tri-iodides from the NQR data of the tri-chloride series.

In particular, the EFG for atomic Cl or I , having electronic configurations $3s^2 3p^5$ and $5s^2 5p^5$, respectively, is given by:

$$eq_{at}(pz \text{ hole}) = \frac{4}{5} e \langle r^{-3} \rangle_n, \quad (4)$$

where n is the principal quantum number of the p shell.

The ratio of the quadrupole coupling constants becomes

$$R_1 = \frac{e^2 q_{at} Q(Cl)}{e^2 q_{at} Q(I)} = \frac{Q(Cl)}{Q(I)} \cdot \frac{\langle r^{-3} \rangle_3}{\langle r^{-3} \rangle_5}. \quad (5)$$

Using the calculated values of $\langle r^{-3} \rangle$ given by Mann⁵ and the experimental values of the quadrupole moments⁹ for Cl^{35} and I^{129} (see Table I), we obtain:

$$R_1 = 0.066 \pm 0.002. \quad (6)$$

| Atom | Configuration | $\langle r^{-3} \rangle$ | Q_{gs} |
|-----------|---------------|--------------------------|----------------------|
| Cl^{35} | $3p^5$ | 6.768695 | $-0.079 \pm 0.004^*$ |
| I^{129} | $5p^5$ | 14.86653 | $-0.55 \pm 0.02^*$ |

Table I - Calculated values of $\langle r^{-3} \rangle$ (atomic units) for chlorine and iodine atoms from Mann⁸ and experimental values of the quadrupole moments (in barns) of Cl^{35} and I^{129} from Nuclear Data tables⁹.

*Rounded-off values for the ground state.

Supported by the data given in Table II, which shows the ratios of the quadrupole couplings of various solid halide compounds to gaseous ones, we make the assumption that this theoretical ratio for atomic quadrupole coupling constants is approximately equal to the molecular one; i.e.,

$$R_2 \equiv \frac{e^2 q_{mol} Q(Cl^{35})}{e^2 q_{mol} Q(I^{129})} \simeq 0.066. \quad (7)$$

Using the quadrupole interaction parameters measured by Carlson and Adams² (Table III), we can estimate the quadrupole coupling for the rare earth iodides. These values are given in Table IV.

| Quadrupole Coupling Ratio | Gas Phase | Solid Phase |
|---|-----------|-------------|
| $\frac{e^2qQ(\text{CH}_3\text{Cl})}{e^2qQ(\text{CH}_3\text{Br})}$ | -0.129 | -0.129 |
| $\frac{e^2qQ(\text{CH}_3\text{Cl})}{e^2qQ(\text{CH}_3\text{I})}$ | 0.039 | 0.039 |
| $\frac{e^2qQ(\text{CH}_3\text{Br})}{e^2qQ(\text{CH}_3\text{I})}$ | -0.299 | -0.299 |
| $\frac{e^2qQ(\text{CF}_3\text{Cl})}{e^2qQ(\text{CF}_3\text{Br})}$ | -0.126 | -0.126 |
| $\frac{e^2qQ(\text{CF}_3\text{Cl})}{e^2qQ(\text{CF}_3\text{I})}$ | 0.036 | 0.038 |
| $\frac{e^2qQ(\text{CF}_3\text{Br})}{e^2qQ(\text{CF}_3\text{I})}$ | 0.289 | 0.292 |

Table II - Pure quadrupole coupling constant ratios of some similar compounds in the gas and solid phases of the halogens Cl^{35} , Br^{79} and I^{127} . The values of the constants are given in table 8.1 of Ref. 13.

| Compound | ν_Q (MHz) | $e^2q_{mol}Q$ (MHz) | η |
|-----------------|---------------------|---------------------|------------------|
| LaCl_3 | $4.084 \pm 0.001^*$ | $8.168 \pm 0.002^*$ | 0.50 ± 0.02 |
| GdCl_3 | $5.23 \pm 0.01^*$ | $10.47 \pm 0.02^*$ | 0.425 ± 0.01 |
| ErCl_3 | $4.445 \pm 0.005^*$ | $8.91 \pm 0.01^*$ | 0.525 ± 0.02 |

Table III - NQR frequencies, $\nu_Q \equiv \frac{1}{2} e^2qQ(1 + \eta^2/3)^{1/2}$, quadrupole coupling constants e^2qQ and η values of Cl^{35} in LaCl_3 , GdCl_3 and ErCl_3 . Ref. 2.

*These values come from interpolation to $\sim 100^\circ\text{K}$.

| Compound | $e^2q_{mol}Q(\text{I } 129)$ (MHz) |
|----------------|------------------------------------|
| LaI_3 | 123 \pm 7 |
| GdI_3 | 158 \pm 19 |
| ErI_3 | 135 \pm 8 |

Table IV - Estimated values of e^2qQ for I^{129} in LaI_3 , GdI_3 and ErI_3 using relation (7) and from Table III.

Such estimates serve as a starting point to a least squares fit to the I^{129} data. This fitting procedure consists of varying the parameters associated with the quadrupole interaction and the isomer shift for I^{129} in order to produce the best possible fit to the data.

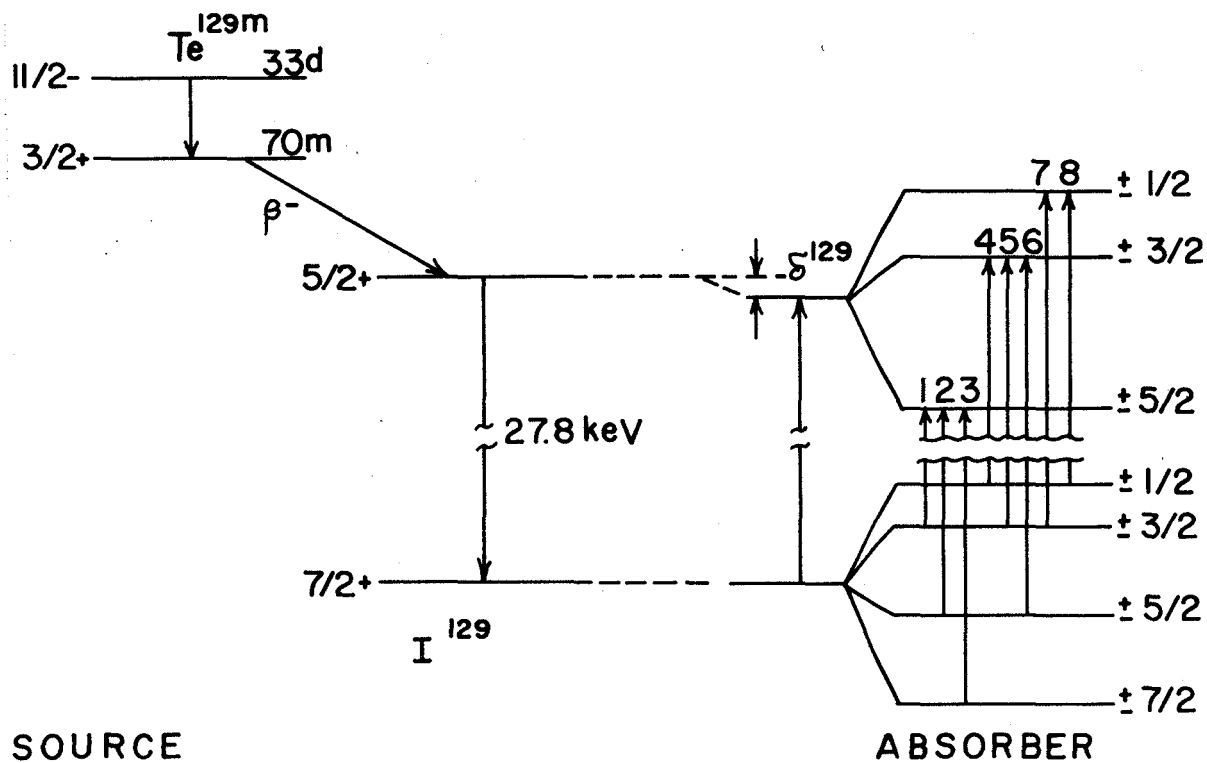


Figure 1 - Energy levels for a Te^{129m} source and an I^{129} absorber. The nuclear level splittings in the absorber are shown assuming eq as positive.

In particular, the absorption spectrum of a iodine 129 compound (with quadrupole interaction), shown in Fig. 1, consists of eight allowed nuclear transitions between the 7/2+ ground to the 5/2+ first excited nuclear state. The line positions are related to the quadrupole coupling, the asymmetry parameter η , and the isomer shift δ by¹⁰:

$$E_{ij} = A\{Rf(I^*, m_i^*, n) - f(I, m_j, n)\} + \delta, \quad (9)$$

where $A = e^2 q Q_{GS}/4$, $f(I, m, n)$ is related to the spin Hamiltonian eigenvalues for the case of non-axial symmetric electric field and R is the quadrupole moment ratio of I^{129} ($= Q_{ES}^*/Q_{GS} = 1.23$)¹¹.

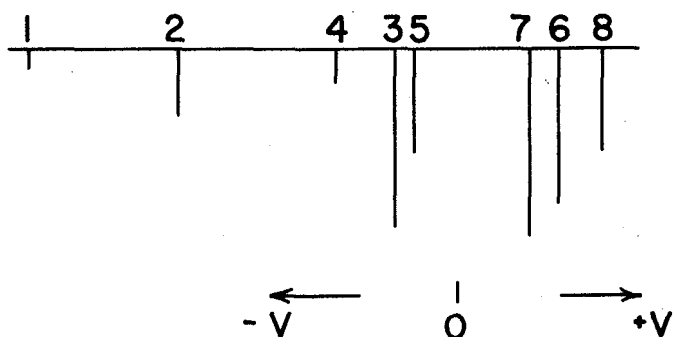


Figure 2 - Line positions of the I^{129} absorption spectrum in velocity units. The conversion factor is c/E_γ , where c is the speed of light and $E_\gamma = 27.8$ keV.

The theoretical Mossbauer absorption spectra consist of a sum of Lorentzian curves with positions and amplitudes represented by the lines in Fig. 2. The intensity and position of these peaks depend on the spin Hamiltonian parameters. In the actual fitting procedure, the position of the absorption lines (and widths) were varied so as to produce the best possible fit to the experimental spectrum. After this adjustment, the values of the quadrupole interaction parameters and isomer shift were extracted.

| Compound | $e^2 q_{mol} Q (I^{129})$ (MHz) | η | δ (mm/sec) |
|----------|---------------------------------|--------|--------------------|
| LaI_3 | -80 ± 8 | 0.20 | -0.285 ± 0.033 |
| GdI_3 | -115 ± 8 | 0.50 | -0.273 ± 0.033 |
| ErI_3 | -144 ± 8 | 0.44 | -0.249 ± 0.033 |

Table V - Estimated values of $e^2 q Q$, η and isomer shift δ for I^{129} in the R. E. tri-iodides, obtained by least squares fitting.

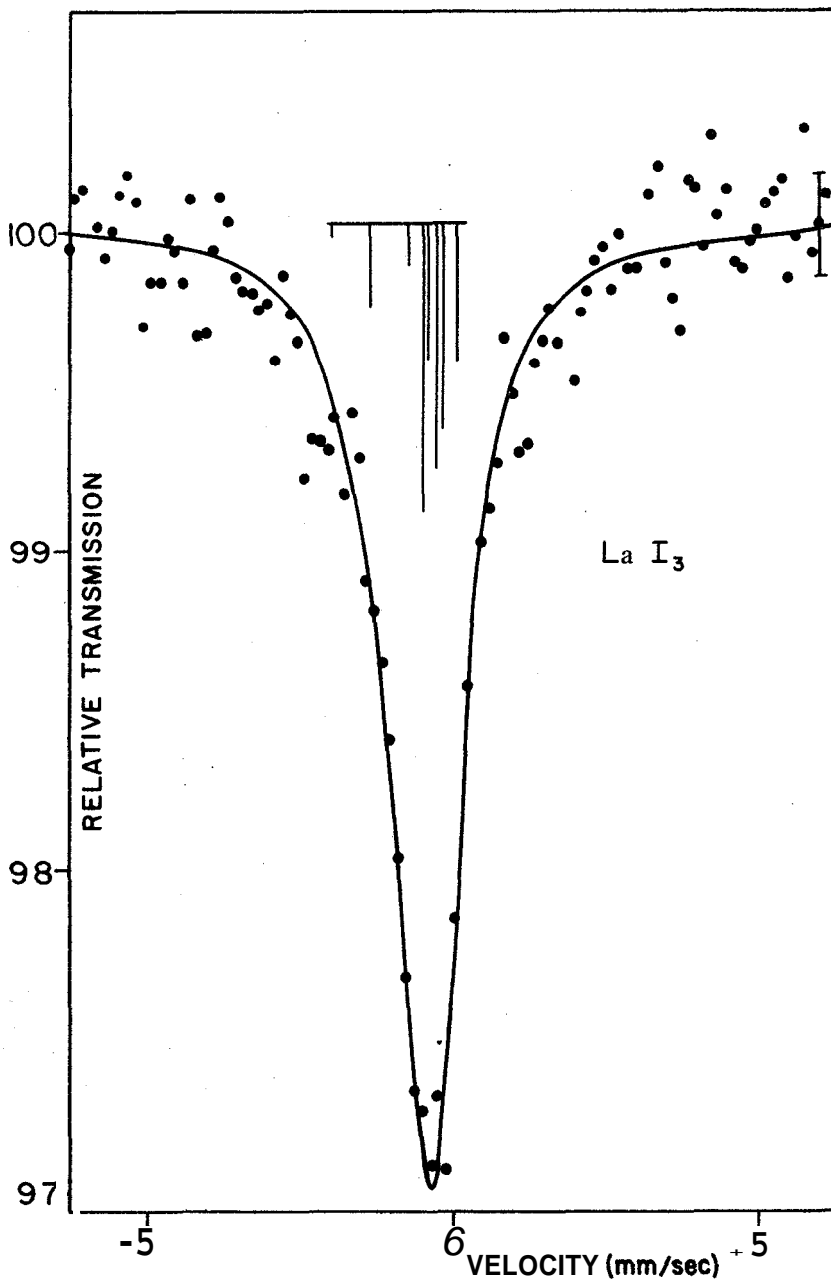


Figure 3 - Experimental Mossbauer spectrum of LaI_3 . The solid line is the theoretical absorption curve obtained by a least squares fitting.

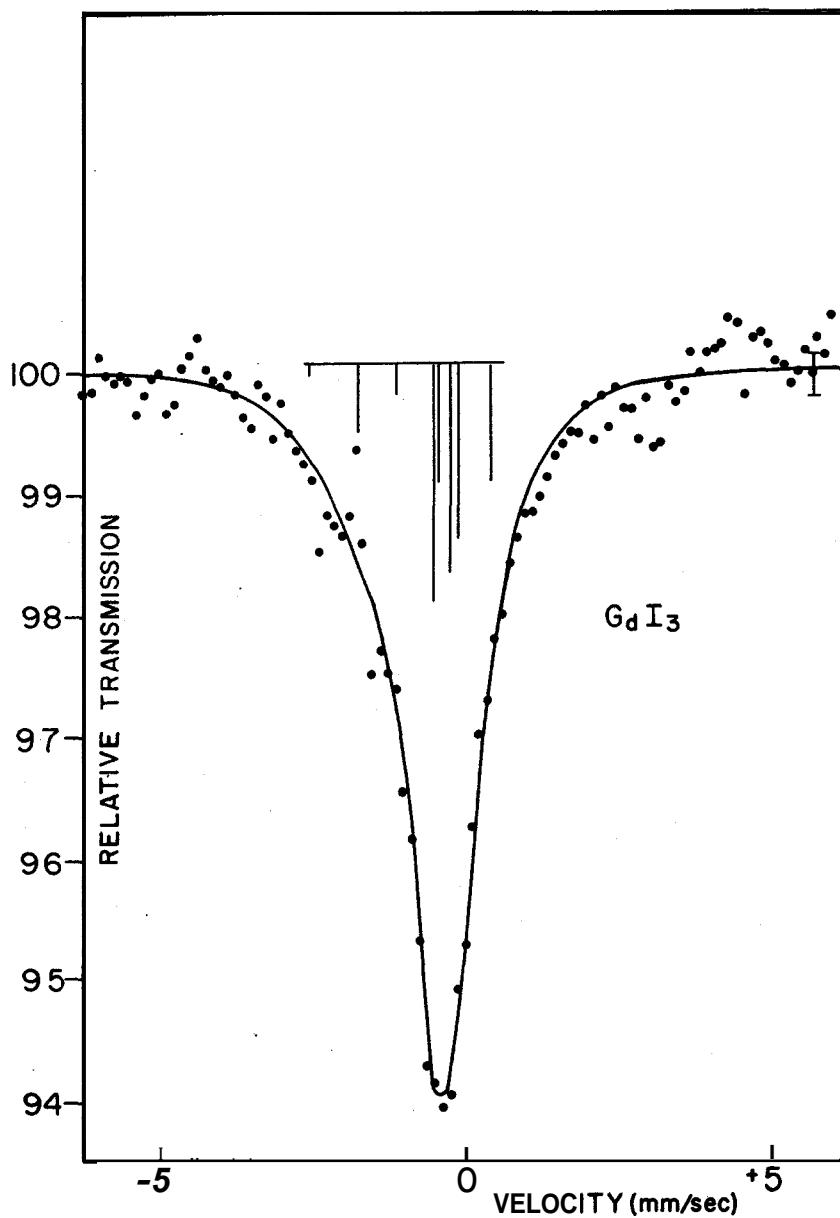


Figure 4 - Experimental Mössbauer spectrum of GdI_3 . The solid line is the theoretical absorption curve obtained by a least squares fitting.

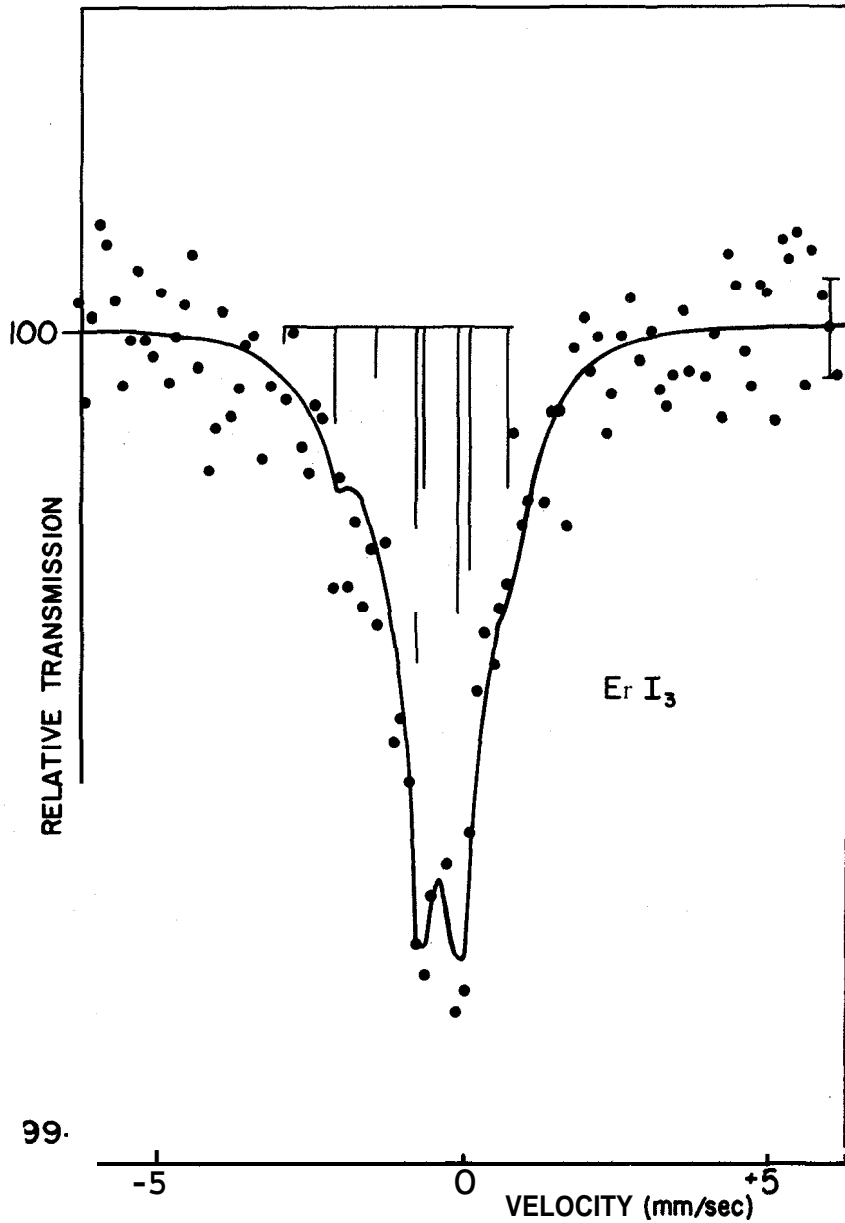


Figure 5 - Experimental Mossbauer spectrum of ErI_3 . The solid line is the theoretical absorption curve obtained by a least squares fitting.

Figures 3,4 and 5 show the comparisons between the theoretical and experimental spectra for the rare earth tri-iodides and Table V contains the final parameters obtained.

These values represent the best overall fits to the data (including the **original** fits with single Lorentzian peaks) consistent with the **idea** of unresolved quadrupole splittings.

3. Interpretation and Conclusions

The experimental **evidence** of atomic EFG in the rare earth tri-iodides of the **type** AI, leads us to consider that covalent effects are present. The electronegativity of iodine is larger than the one of the rare earth elements, which implies that the isomer shift is related only to the number of p-holes, h . Both aspects suggest that the chemical bonding can be understood in terms of the description of orbital overlap given by Owen and **Thornley**⁴. The s and d electrons from the **outer** electronic configuration of La , Gd and Er , hybridize in the bonding with iodine 5-p electrons **leaving** a p-hole partially occupied. In this **sense** U_p is given by $(1-x)$, where x is the amount of hybridization between the s and d electrons from the ligands. This approach **differs** from the one given by Townes and **Daily**¹², where s and d orbitals hybridization of the same atom are considered. However, from either approach, the expression for U_p is the same.

The quantity U_p is related to the p electron distribution in the x , y and z directions (p_x , p_y and p_z populations) by the following expression:

$$U_p = -U_z + \frac{1}{2}(U_x + U_y), \quad (8)$$

where U_z , U_x and U_y are related to the asymmetry parameter, η , and the number of p holes in the $5s^2 5p^6$ configuration by:

$$\eta = \frac{3}{2} \frac{U_x - U_y}{U_p}, \quad (9)$$

$$h_p = 6 - (U_x + U_y + U_z). \quad (10)$$

Using relations(1), (3), (8)-(10)and Table V, taking $e^2 q_{ar} Q$ as -1223.5 MHz, and the relationship between h and the isomer shift for I^{129} , namely

$$\delta = 1.36 h - 0.54 \text{ (mm/s)},$$

we constructed Table VI.

| Compound | U_p | h_p | U_x | U_y | U_z |
|----------------|-------|-------|-------|-------|-------|
| LaI_3 | 0.07 | 0.18 | 1.96 | 1.95 | 1.89 |
| GdI_3 | 0.09 | 0.20 | 1.98 | 1.95 | 1.87 |
| ErI_3 | 0.12 | 0.21 | 1.99 | 1.95 | 1.85 |

Table VI - Estimated values U_p , h_p , V_p , U_x , U_y and U_z for I^{129} in LaI_3 , GdI_3 , ErI_3 using relations (1), (3), (8) - (10) and Table V. The value of e^2qQ is - 1223 MHz, accordingly to (r⁻¹) and $Q(I^{129})$ from Table I.

The large ionicity, ~ 0.80 , is consistent with the ionic character of these crystals, ~ 0.75 . The fractional importance of the ionic bond $x \approx 90\%$, leaving $1-x \approx 10\%$ fractional importance for the covalent bond.

The amount of hybridization that accounts for covalent effects changes from bond to bond and no simple rules are yet known. If we assume that the bonding in the rare earth tri-iodide compounds is simple covalent, the number of unbalanced p-electrons would be given³ by $U_p = 1 - s + d$, which means a hybridization between s and d electronic wave functions of the rare earth ligands. It should be noted that we are using a hybridization due to an orbital overlapping of the wave functions of the ligands instead of a hybridization of the s and p type wave functions of the iodine as described by Owen and Thornley⁴. The average numerical value derived for U_p (~ 0.10) can be understood as resulting from an admixture of 60% of s -wave function and 30% of d -wave function of the ligands to the p -wave function of the iodine. Small deviations can be explained by the presence of f -electrons in the bonding. The small departure from complete ionicity and the estimated values for the quadrupole coupling explain quite reasonably the unresolved Mossbauer spectra for the I^{129} compounds of rare earths.

From these studies, we can estimate the NQR frequencies for the tri-iodides reported in this paper. In particular, associated with the $5/2$ nuclear ground state of I^{127} are the two NQR transitions $5/2 \rightarrow 3/2$ and $3/2 \rightarrow 1/2$, with the NQR frequencies given by¹³:

$$\begin{aligned}
 \nu_Q^1 &= \frac{3e^2 qQ}{10} \left(1 - \frac{11}{54} \eta^2 \right), \\
 \nu_Q^2 &= \frac{3e^2 qQ}{20} \left(1 + \frac{5}{54} \eta^2 \right),
 \end{aligned} \tag{11}$$

respectively.

| Compound | $\nu_Q(5/2 \rightarrow 3/2)$ MHz | $\nu_Q(3/2 \rightarrow 1/2)$ MHz |
|------------------------|----------------------------------|----------------------------------|
| LaI₃ | 16.7 | 8 |
| GdI₃ | 23 | 12 |
| ErI₃ | 29 | 15.5 |

Table VII - Estimated I^{127} NQR frequencies, ν_Q , given by relations (11) and the $e^2 qQ$'s from Table V. The conversion from I^{129} to I^{127} is given by the ratio of the ground state quadrupole moments $Q(I^{129})/Q(I^{127}) = 0.701$ from Ref. 7.

From Table V, relations (11) and using the measured ratio of the ground state quadrupole moments of I^{129} and I^{127} , $\frac{Q(I^{129})}{Q(I^{127})} = 0.7017$, one obtains the estimated frequencies given in Table VII.

An experimental evaluation of these frequencies through NQR measurements would be complementary to this work and would provide additional confirmation to the present approach to understand the quadrupole interaction in these almost "ionic" compounds.

One of us (M. I. da Costa, Jr.) thanks Tullio Sonnino for suggesting the experimental work on I^{129} compounds. We thank John D. Rogers and Celso Müller for supplying the least squares fit program with display on line.

References and Notes

1. M. I. da Costa Jr., E. F. R. Fraga and T. Sonnino, J. Chem. Phys. 52, 161 (1970).
2. E. H. Carlson and H. S. Adams, J. Chem. Phys. 51 388 (1969).
3. C. H. Townes and A. L. Schawlow, Microwave Spectroscopy (McGraw-Hill, New York, 1955), Chap. 9.
4. J. Owen and J. H. M. Thornley, Rep. Prog. Phys. XXM (1966) II.
5. B. A. Goodman, N. N. Greenwood and G. E. Turner, Chem. Phys. Letters, 5 181 (1970).
6. We wish to thank Adalberto Vasquez for supplying the monopole sum calculation program.
7. M. Pasternak and S. Bukshpan, Phys. Rev. 163 297 (1967).
8. Joseph B. Mann, "Atomic Structure Calculations II Hartree-Fock Wave Functions and Radial Expectation Values: Hydrogen to Lawrencium", LA-3691, Los Alamos Sc. Lab. (1968).
9. Nuclear Data Tables, A5, 433-612 (1969).
10. M. Pasternak, thesis, Rehovot, Israel (1967), unpublished.
11. D. W. Hafemeister, G. de Pasqualli and H. de Waard, Phys. Rev. 135B, 1089 (1964).
12. C. H. Townes and B. P. Dailey, J. Chem. Phys. 17 782 (1949).
13. E. A. C. Lucken, Nuclear Quadrupole Coupling Constants, (Academic Press, New York, 1969), Chap. 8.