

# Rare-Earth Tri-iodides—Mössbauer Effect Using $^{129}\text{I}$

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$(\chi_1)^2$ . Within each treatment, electron correlation causes an increase in density both "behind" and around each nucleus at the expense of the midbond region. Such a movement of charge, greatest for  $(\sigma, \sigma')$ , is in keeping with the tendency, observed earlier, for  $R_{\text{theoret}}$  to increase as we introduce electron correlation. Bender and Davidson<sup>6</sup> found that correlation effects within HeH and LiH caused a noticeable decrease in electron repulsion energy along with a smaller, but positive, change in kinetic energy; only a slight increase was observed in the nuclear attraction energy. We found that corresponding energy changes occurred within HeH<sup>+</sup>.

Difference maps  $\Delta\rho(\vec{r})$  in Fig. 1(c) and 1(d) are for molecular formation when  $R \approx R_{\text{theoret}}$ . Figure 1(c) is the difference between densities obtained from HeH<sup>+</sup>  $(\sigma, \sigma')$  and the corresponding wavefunction<sup>5</sup> for He(1s, 1s'). The contours in Fig. 1(d) are derived<sup>5</sup> from the CI molecular function<sup>4</sup> and a CI treatment<sup>4</sup> for He. Each model predicts a decrease in charge at the He nucleus. In Fig. 1(c), the maxima and minima are located too close to He by comparison with the CI treatment indicating,<sup>7</sup> perhaps, why  $R_{\text{theoret}}(\sigma, \sigma')$  is too large. Expanding  $(\sigma, \sigma')$  in terms of Slater-type orbitals reveals that coefficients of configurations containing higher-angular orbitals involve increasing powers of  $\lambda$  and  $\mu$  which, being  $<1$ , limits the density changes caused by the proximity of the proton. This is reflected in our energy for HeH<sup>+</sup>. Configurations  $(1s, 2p_\sigma)$  and  $(1s, 3d_\sigma)$  caused significant lowering in the CI energy,<sup>4</sup> however, the effectiveness of such terms in  $(\sigma, \sigma')$  is restricted by a  $\mu^2$  dependence.

Although several interesting points emerge from this analysis, it primarily highlights features of  $(\sigma, \sigma')$  and its associated basis orbitals which should aid future application.

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<sup>1</sup> E. Scrocco and J. Tomasi, *Mol. Phys.* **4**, 193 (1961). K. C. Bhalla and P. G. Khubchandani, *Mol. Phys.* **9**, 229, 291 (1965).

<sup>2</sup> K. E. Banyard and M. R. Hayns, *Mol. Phys.* **15**, 615 (1968); see function  $\tilde{E} - (\sigma, \sigma')$  and function  $A - (\sigma)^2$ .

<sup>3</sup> Atomic units are used throughout this work.

<sup>4</sup> J. D. Stuart and F. A. Matsen, *J. Chem. Phys.* **41**, 1646 (1964).

<sup>5</sup> C. C. Baker and K. E. Banyard, "Molecular Formation and Electron Correlation in HeH<sup>+</sup>" (to be published).

<sup>6</sup> C. F. Bender and E. R. Davidson, *J. Phys. Chem.* **70**, 2675 (1966).

<sup>7</sup> R. F. W. Bader, I. Keaveny, and P. E. Cade, *J. Chem. Phys.* **47**, 3381 (1967).

### Rare-Earth Tri-iodides—Mössbauer Effect Using <sup>129</sup>I\*

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We report here some preliminary results on rare-earth tri-iodides using Mössbauer effect in <sup>129</sup>I. Absorbers

TABLE I. Experimental results.

Absorber	i.s. (mm/sec)
CuI	-0.382±0.001 <sup>a</sup> -0.382±0.004
LaI <sub>3</sub>	-0.252±0.012 <sup>b</sup>
GdI <sub>3</sub>	-0.378±0.014 <sup>b</sup>
ErI <sub>3</sub>	-0.294±0.028 <sup>b</sup>

<sup>a</sup> Reference 5.

<sup>b</sup> Isomer shift in respect to the standard source ZnTe for LaI<sub>3</sub>, GdI<sub>3</sub>, ErI<sub>3</sub>.

of LaI<sub>3</sub>, GdI<sub>3</sub>, and ErI<sub>3</sub> were investigated, as part of a systematic study of all the lanthanides.

The lanthanide tri-iodides crystallize either in orthorhombic structure<sup>1,2</sup> as LaI<sub>3</sub>, or in a hexagonal structure as in the case of GdI<sub>3</sub> and ErI<sub>3</sub>.

These compounds were prepared by the method of Asprey *et al.*<sup>1</sup> by reacting the metal with a stoichiometric amount of HgI<sub>2</sub> in vacuum. The mercuric iodide was prepared using a solution of sodium iodide (129 isotope) purchased from Oak Ridge National Laboratory.

The Mössbauer source was in the standard form of ZnTe and the isomer <sup>129m</sup>Te ( $t_{1/2} = 33d$ ) was used, obtained from irradiation of 100 mg of <sup>128</sup>Te in the high reactor flux of the Radiochemical Centre Amersham, for 21 days.

Purification and source synthesis were done along the lines described by Sanders and de Waard.<sup>3</sup>

The apparatus for Mössbauer spectroscopy is a

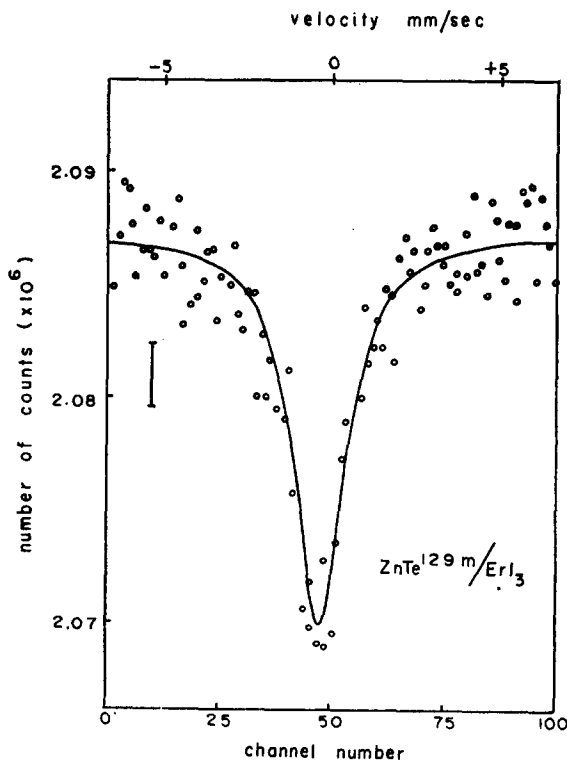


Fig. 1. The Mössbauer effect absorption spectrum of ErI<sub>3</sub>.

forward and back constant acceleration developed in our laboratory.<sup>4</sup>

All measurements were done with source and absorbers at liquid nitrogen temperature.

To check our source, a spectrum using a Cu<sup>129</sup>I absorber was also detected. This gives an isomer shift (i.s.) of  $-0.382 \text{ mm/sec} \pm 0.004$  which agrees perfectly with the value obtained previously with a different system in another laboratory using <sup>66</sup>ZnTe and where the whole source was irradiated in the neutron flux of the reactor<sup>5</sup> to produce <sup>129</sup>Te ( $t_{1/2} = 77 \text{ min}$ ). The source recoilless fraction  $f_s$ <sup>6</sup> was also checked and found  $0.059 \pm 0.005$  using Cu<sup>129</sup>I as absorber.

The value of  $f_a$  for CuI was taken as 0.19.<sup>7</sup> We then found that  $f_s(^{66}\text{Zn}^{129}\text{Te})/f_s(\text{Zn}^{129\text{m}}\text{Te}) = 3.93 \pm 0.4$  in agreement with the value  $3.56 \pm 0.11$  of Ref. 3.

The Mössbauer effect spectra of LaI<sub>3</sub>, GdI<sub>3</sub>, and ErI<sub>3</sub> show an unsplit absorption peak, indicating the absence of a detectable quadrupole or magnetic interaction. A typical spectrum is shown in Fig. 1 and a summary of the results is given in Table I.

The isomer shift is negative and in the same range of values as for the alkali iodides. The absence of quadrupole interaction is an unexpected result, as the iodide atom in the crystal is in a site of low symmetry, for the two structures.

In our previous results<sup>8,9</sup> it was shown that the relationship between the i.s. and quadrupole coupling  $e^2qQ$  is almost linear for <sup>129</sup>I.

Deviations from linearity are due to effects which, for negatively charged iodine, all reduce the quadrupole interaction: (1) participation of  $s$  electrons in the bond ( $sp$  hybridization), (2)  $\pi$  character of the bond, (3) ionicity of the bond.

It is then possible that  $e^2qQ$  is of the same order of magnitude or even less than the experimental linewidth of  $\approx 20 \text{ Mc/sec}$ .

On the other hand it is also known that rare-earth salts are almost ionic and so the electronic structure of iodine could be very similar to that of I<sup>-</sup> characteristic of the alkali iodides<sup>10</sup> as the value of isomer shift indicates.

The reason for the difference in the value of i.s. among the three compounds is not clear and more work will be necessary to understand the point. Measurements at liquid helium and intermediate temperatures are in progress.

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## Total EPR Absorption Intensity from Powders of $S' = \frac{1}{2}$ Systems with Rhombic $g$ Tensors

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Many applications of EPR spectroscopy require measurements of signal intensities, as these give a measure of the number of unpaired spins in the samples. This is particularly true in biochemical applications, where the conclusions drawn from a signal often are very dependent on the intensity. When the intensities of two signals with different  $g$  values are compared, they must be corrected for the difference in the transition probabilities. For powders of frozen solutions a suitable average of this probability must be used. In an earlier publication<sup>1</sup> we have given the appropriate correction factor for  $S' = \frac{1}{2}$  systems with axial  $g$  tensors, and this is now extended to the case of rhombic  $g$  tensors.

The transition probability averaged over all orientations of the microwave field perpendicular to the static field has been given by Holuj<sup>2</sup> and later by Pilbrow.<sup>3</sup> With the static field in the direction  $(\vartheta, \varphi)$  this probability is<sup>3</sup>

$$g^2 = [g_x^2 g_y^2 \sin^2 \vartheta + g_y^2 g_z^2 (\sin^2 \varphi + \cos^2 \vartheta \cos^2 \varphi) + g_z^2 g_x^2 (\cos^2 \varphi + \cos^2 \vartheta \sin^2 \varphi)] / 2g^2, \quad (1)$$

where  $g$  is the  $g$  value in this particular direction [note that the denominator of Eq. (1) is missing in Ref. 3]. To get the total intensity of a powder we have averaged  $g^2$  over all directions by numerical integration. The result is given in the form

$$g^2_{\text{av}} = g_y^2 \tau (g_x/g_y, g_x/g_y), \quad g_x < g_y < g_z. \quad (2)$$

In this relation  $\tau$  is a function of the  $g$ -value ratios and can be read from Fig. 1.

The expression for the magnetic susceptibility of a powder contains the average of the squares of the  $g$  values. We have found that, even with rather large anisotropies, the square of the  $g$ -value average gives a good approximation of the total EPR intensity which is much better than that obtained with the average of the squares. Thus, we have approximately

$$g^2_{\text{av}} = \frac{1}{3} (g_x + g_y + g_z)^2. \quad (3)$$